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DOI: https://doi.org/10.1515/MGMC.1996.19.12.769

SYNTHESIS OF CHIRAL ALLENES BY PETERSON-TYPE OLEFINATIONS

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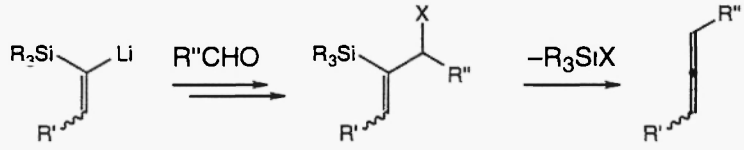
Abstract

Chiral 1,3-disubstituted allenes have been prepared by means of a *Peterson*-type elimination in yields as high as 95%. To obtain optically active allenes, the [(benzyloxy)methyl](*tert*-butyl)methylsilyl group was used as the chiral auxiliary to get an optically enriched elimination precursor. Unfortunately, the elimination reaction with this compound to the respective allene was not stereospecific. Only racemic allene was obtained, probably due to a reaction course *via* a carbocationic intermediate (E_1 rather than E_2 mechanism).

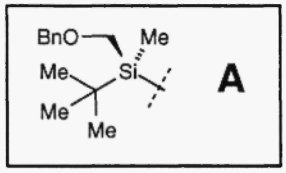
Introduction

The chemistry of allenes has witnessed an immense growth over the past few decades. Allenes not only gained importance as synthetic intermediates for a variety of transformations but they also exhibit interesting and unique physiological properties[1]. It is not surprising, therefore, that a rather broad arsenal of methods for the preparation of allenes and cumulenes have been elaborated. Among those, also a *Peterson*-type of olefination was studied as a means to introduce the two cumulated double bonds[2-4]: α-litiated vinylsilanes **1** were coupled with aldehydes to silyl-substituted allyiic alcohols **2** (X = OH), which were expected to deliver allenes **3** by 1,2-elimination of R_3SiOH (*Scheme 1*). However, the treatment of **2** (X = OH) with base or fluorides resulted only in hydrodesilylation[4, 5], and the elimination of R_3SiX (X = O-acyl or halogen) under the influence of fluorides was found to proceed but sluggishly[2, 3]. Nevertheless, *Torres* et al. have used the method for their preparation of an enantiomerically enriched chiral allene, which was obtained, though, not only with poor chemical yield but also with low stereoselectivity[6].



1 **2** **3**

(X = OH, O-acyl, Hal)



Scheme 1

In connection with our ongoing studies of diastereoselective reactions using the chiral alkoxymethyl-substituted silicon group **A** as a stereochemical director[7] and inspired by the results of *Torres* et al., we became interested in the re-investigation of the above-mentioned *Peterson*-type

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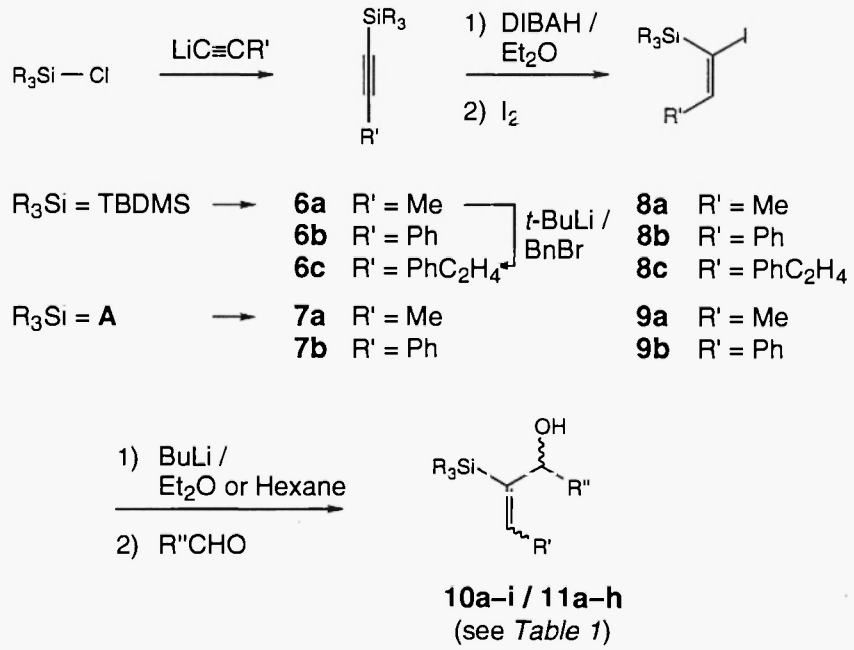
1) Part of the planned PhD thesis of *S. B.*, University of Zurich, Switzerland.

process. We particularly aimed at an optimization of the reaction conditions for the elimination step—not only to obtain higher yields of the allenes **3** but also in the hope to ensure better stereoselectivities.

Results and Discussion

The achiral and the racemic silylated alcohols **10a–h** and **11a–h** that we used for this study were prepared from the corresponding chlorosilanes **4** and **5**, respectively. Reaction of **4** and **5** with acetylides led to the alkynylsilanes **6a,b** and **7a,b**, which were converted to the vinyl iodides **8a–c** and **9a,b** by a sequence of hydroalumination and iodination (for **8c** preceded by the deprotonation and benzylation of **6a** to **6c**). Metal-halogen exchange and reaction with the pertinent aldehydes delivered the desired products **10a–i** and **11a–h** in good yields (*Scheme 2*, *Table 1*). The stereochemistry around the double bonds in the compounds of the type **10** and **11** could be controlled in two ways: by the proper choice of the reaction conditions either in the hydroalumination step or in the metal-halogen exchange. Hydroaluminations of alkynylsilanes with diisobutylaluminum hydride (DIBAH) in hexane are known to give rise to (*E*)-configured α-silylalanes, whereas the reactions performed in the presence of donating additives or solvents generally deliver the (*Z*)-configured products[8]. In fact, the alkynylsilyl-substituted *tert*-butyldimethylsiliyl (TBDMS) compounds **6a–c** gave—depending solely on the reaction conditions—rise to either of the two possible double bond isomers, as shown in a separate study[9]. The reaction of **6a–c** with DIBAH in Et_2O at –78°C followed by quenching with I_2 produced the (*E*)-configured iodovinyl silanes **8a–c**; likewise, the corresponding (*Z*)-configured compounds could be obtained when the reactions were performed in hexane. Starting from the chiral alkoxymethyl-substituted silicon compound **7a,b**, on the other hand, only (*E*)-configured vinyl iodides **9a,b** could be obtained, irrespective of the reaction conditions used. Probably due to internal complexation of the aluminum with the benzyloxymethyl portion of the silicon moiety, the isomerization of the initially formed *syn*-addition product to the (*E*)-configured α-metallated vinylsilane was inhibited.



Scheme 2

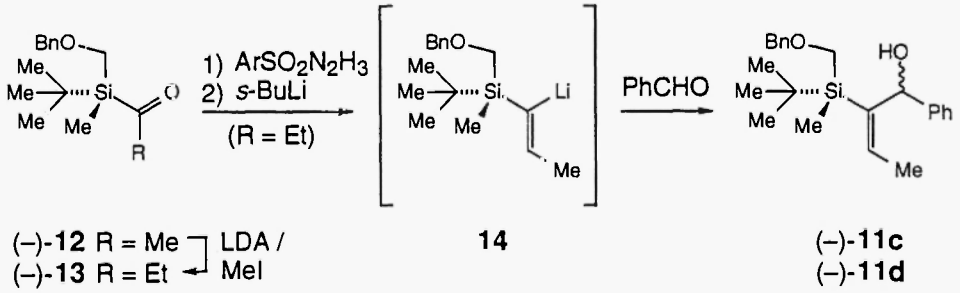
Nevertheless, for both types of silanes (R_3Si = TBDMS or **A**) both double bond isomers of the silylated allylic alcohols of the types **10** and **11** could be attained. In accordance with published results[10, 11], we found that the (*Z*)-configured α-silylated vinyllithium intermediates, obtained from

Table 1: Preparation of the Silyl-Substituted Allylic Alcohols **10a–i** and **11a–h**.

Entry	Educt	Product					
	No	No	R_3Si	R'	R'''	Double Bond	Yield (%)
1	**8a**	**10a**	TBDMS	Me	Ph	*Z*	81
2	**8a**	**10b**	TBDMS	Me	Ph	*E*	74
3	**8b**	**10c**	TBDMS	Ph	Et	*Z*	87 (10:1)[a]
		10d	TBDMS	Ph	Et	*E*	
4	**8b**	**10e**	TBDMS	Ph	Ph	*Z*	82
5	**8b**	**10f**	TBDMS	Ph	Ph	*E*	79
6	**8b**	**10g**	TBDMS	Ph	i-Pr	*Z*	82
7	**8c**	**10h**	TBDMS	PhC_2H_4	Ph	*Z*	83 (15:1)[a]
		10i	TBDMS	PhC_2H_4	Ph	*E*	
8	**9a**	**11a**	**A**	Me	Ph	*Z*	69 (2:1)[a]
		11b	**A**	Me	Ph	*Z*	
9	**9a**	**11c**	**A**	Me	Ph	*E*	60 (5:7)[a]
		11d	**A**	Me	Ph	*E*	
10	**9a**	**11e**	**A**	Me	i-Pr	*Z*	93 (1:2)[a]
		11f	**A**	Me	i-Pr	*Z*	
11	**9b**	**11g**	**A**	Ph	Ph	*E*	80 (5:6)[a]
		11h	**A**	Ph	Ph	*E*	

[a] The reactions were performed under conditions to obtain both isomers (see. *Exp. Part*)

the respective (*E*)-configured vinyl iodides, can be isomerized to the more stable (*E*)-configured analogs. The rate of isomerization of the α-metallated vinyl silicon species depends crucially on the reaction temperature and the solvent: generating and keeping the vinyllithium species in hexane at –80°C (or below) allowed to retain their double bond geometries; warming them up to –5°C or holding them in a donating solvent like Et_2O or THF for a few hours, resulted in partial or complete double bond inversion. Thus, in general both double bond isomers of the compounds of the type **10** and **11** could be prepared from the corresponding common (*E*)-configured vinyl iodides of the type **8** or **9** by the proper choice of the reaction conditions (see *Exp. Part*). A problem, though, arose still in the preparation of the (*Z*)-configured alkoxymethyl-substituted silicon compounds of the type **11**: since these compounds possess internally a donating ether functionality, it was rather arduous to retain the doble bond geometry of the respective (*Z*)-configured vinyllithium species after the metal-halogen exchange; the reaction temperature had to be strictly kept below –90°C to minimize double bond inversion. Even this was not sufficient for the reaction with the phenyl-substituted derivative **9b**, whose corresponding lithiated species isomerized especially readily. For this starting material, the double bond geometry could be retained to only 30% at its best.



(–)-**12** R = Me, (–)-**13** R = Et ← LDA / MeI

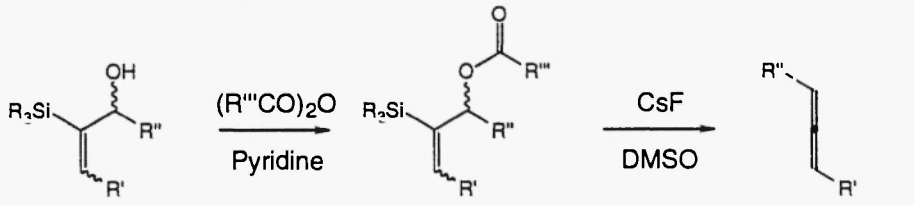
14

(–)-**11c**, (–)-**11d**

Scheme 3

Optically active **11c,d** were obtained by a different route (*Scheme 3*). Enantiomerically enriched acetylsilane (–)-**12** (>96% ee)[12] was alkylated with methyl iodide *via* the lithium enolate, and the resulting ethyl silyl ketone (–)-**13** was converted to the corresponding α-lithiated vinyl-

silane **14** by the *Shapiro* reaction. Addition of the organolithium species to benzaldehyde afforded the two alcohols (–)-**11c** and (–)-**11d**. The stereoselectivity in the addition reaction proved to be disappointingly low (dr *ca.* 1.2 : 1). However, oxidation of the chiral alcohols of the type **11** to the corresponding ketones, followed by re-reduction with $LiAlH_4$, produced one of the respective alcohols with virtually complete stereoselection.



10a–h / 11a,c,e **15a–m / 16a–c** (see *Table 2*) **17a–e** (see *Table 2*)

Scheme 4

Allene formation was optimized with several O-acyl compounds of the type **15** and **16** prepared from the parent alcohols of the type **10** and **11** (*Scheme 4* and *Table 2*). Trifluoroacetates as **15a** (R'''= F_3C), which were used in preceding investigations[2, 3, 6], proved to be tedious to access, and their reaction with several fluorides did not provide any allenes. Instead, as shown exemplary with the transformation of **15a**, the reaction with, *e.g.*, CsF in DMSO gave rise to negliable amounts of allene **17a**; the major products being the 'hydrolysis' compounds **11a** and **11b** (!).

Table 2: Conversion of the Silyl-Substituted Allylic Alcohols **10a–h** and **11a,c,e** to the Allenes **17a–e**.

Entry	*Educt*						*Conditions*		*Product*	
	No	R_3Si	R'	R''	Double Bond	R'''	T (°C)	t (h)	No	Yield (%)
1	**15a**	TBDMS	Me	Ph	*Z*	F_3C	23	3	**17a**	2
2	**15b**	TBDMS	Me	Ph	*Z*	Me	140	6	**17a**	55
3	**15c**	TBDMS	Me	Ph	*Z*	H_2ClC	75	48	**17a**	31
4	**15c**	TBDMS	Me	Ph	*Z*	H_2ClC	100	8	**17a**	33
5	**15c**	TBDMS	Me	Ph	*Z*	H_2ClC	140	1.25	**17a**	50
6	**15d**	TBDMS	Me	Ph	*E*	Me	120	96	**17a**	30
7	**15e**	TBDMS	Ph	Et	*Z*	Me	100	2.5	**17b**	95
8	**15f**	TBDMS	Ph	Et	*Z*	H_2ClC	100	1.5	**17b**	82
9	**15g**	TBDMS	Ph	Et	*Z*	HCl_2C	100	0.8	**17b**	64
10	**15h**	TBDMS	Ph	Et	*E*	H_2ClC	100	21	**17b**	57
11	**15i**	TBDMS	Ph	Ph	*Z*	Me	120	1	**17c**	71
12	**15j**	TBDMS	Ph	Ph	*E*	Me	120	96	**17c**	25
13	**15k**	TBDMS	Ph	i-Pr	*Z*	HCl_2C	100	120	**17d**	<2
14	**15l**	TBDMS	PhC_2H_4	Ph	*Z*	Me	120	10	**17e**	71
15	**15m**	TBDMS	PhC_2H_4	Ph	*E*	H_2ClC	120	2	**17e**	60
16	**16a**	**A**	Me	Ph	*Z*	Me	100	24	**17a**	50
17	**16b**	**A**	Me	Ph	*E*	Me	120	48[a]	**17a**	20
18	**16c**	**A**	Me	i-Pr	*Z*	Me	120	48[b]	**17d**	0[b]

[a] Not complete conversion; [b] No reaction.

The formation of allene was successfully realized with compounds of the type **15** and **16** that possess less potent leaving groups. Since allenes decompose readily upon prolonged heating, however, the choice of the proper reaction conditions to secure a rapid conversion the acyl

compounds was crucial. Best results were obtained when the least-activated acetates of the type **15** or **16** possessing the (*Z*)-configured double bond (*Entries 2, 7, 11, 14*, and *16*, *Table 2*) were treated with fluorides in DMSO at 100–140°C for several hours. Yields of up to 95% (*Entry 7*, *Table 2*) of the parent allenes were gained, which is a remarkable improvement as compared to earlier attempts that delivered allenes with 60% yield at their best[2, 3]. Though the reaction rates were higher with starting compounds possessing more activated groups (*cf.* reactions of **15c**, *Entries 3–5* , *Table 2*), the chloro- and dichloroacetates gave still lower yields of the desired allenes due to more side reactions.

Much to our disappointment, the fluoride treatment of optically active silane (–)-**16b** gave the corresponding allene **17a** in low yields and as a racemate only (*Entry 17*, *Table 2*). The earlier results of *Torres* et al.[6], who obtained the same product in 18% ee (assumingly by an *anti*-elimination), could not be verified with our compound. Supposedly, the formation of the allenes proceeds mainly by an E_1 rather than an E_2 mechanism. The E_1 mechanism is probably particularly favored for the (*E*)-configured starting materials, where the transition states for concerted E_2 elimination processes are strongly disfavored due to large $A_{1,3}$ strain. The E_2 mechanism could, however, still be preferred for the (*Z*)-configured elimination precursors. The reaction course by an E_2 mechanism can be the explanation for the fact that the (*Z*)-configured silylated alkenes **15** are converted markedly faster to the corresponding allenes of the type 17 as compared to the (*E*)-configured counterparts (*cf., e.g., Entries 5/6, 11/12, 14/15,* and *16/17*). Since optically active (*Z*)-configured acetates of the type **16** are not accessible, however, this hypothesis cannot be proven momentarily.

Acknowledgement: We thank the members of our analytical laboratories for their excellent services and the *Swiss National Science Foundation* for their generous financial support. We are especially grateful to Prof. Dr. *M. Hesse* who provided us with laboratory space, equipment, and regular occasions for scientific discussions.

Experimental Part

General. Unless otherwise stated: all organic solvents were distilled prior to use. For the reactions THF and Et_2O were dried over Na/ketyl. All reactions were carried out under a blanket of Ar. Soln. for workup procedures were prepared in deionized H_2O. Chromatography: silica gel *Merck 60* (40–63 μm). M.p.: *Mettler FP-5/FP-52*. IR Spectra: *Perkin-Elmer 781*; as films between NaCl plates; data in cm^{-1}. ^1H NMR: at 300 MHz in $CDCl_3$; *Bruker AC-300*; δ in ppm rel. to $CHCl_3$ ($\delta = 7.26$), J in Hz. ^{13}C NMR: at 75.6 MHz in $CDCl_3$; *Bruker ARX-300*; δ in ppm rel. to $CHCl_3$ ($\delta = 77.0$), multiplicities from DEPT-135 and DEPT-90 experiments; CI-MS (chemical-ionization mass spectrometry): *Finnigan MAT SSQ 700* or *Varian MAT 711i;* reactant gas: NH_3; data in *m/z.*

1. ***Preparation of Alkynylsilanes.*** — 1.1. *(*tert*-Butyl)dimethyl(prop-1-ynyl)silane* (**6a**). Propyne was passed through a solution of BuLi (10 ml, 2N in pentane) in hexane (10 ml) at –78°C until the solution turned into a white gel-like solid that was dissolved by addition of THF (10 ml). It was cooled to –78°C and *tert*-butyl(chloro)dimethylsilane (**4**, 2.13 g, 14.13 mmol, dissolved in 10 ml of THF) was added dropwise. The temperature was slowly raised to 23°C (2 h), and the solution was stirred for an additional 16 h. It was re-cooled to –50°C and quenched with 10% aqueous HCl solution The aqueous layer was extracted with Et_2O, and the combined organic phases were dried over $MgSO_4$ and evaporated. The crude product gave after distillation (bulb-to-bulb, 70°C/10^{-3} torr) **6a** (1.67g, 10.84 mmol, 70%) as a colorless oil. IR ($CHCl_3$): 3000*w*, 2950*s*, 2930*s*, 2890*m*, 2860*s*, 2180*s*, 1470*m*, 1460*m*, 1410*w*, 1390*w*, 1360*w*, 1250*s*, 1025*s*, 1010*m*, 940*w*, 840*s*, 820*s*, 810*s*. ^1H NMR: 1.89 (*s*, *Me*C≡); 0.93 (*s*, *t*-Bu); 0.08 (*s*, Me_2Si). ^{13}C NMR: 103.3 (*s*, Me*C*≡); 81.7 (*s*, SiC≡); 26.0 (*q*, *Me*$_3$C); 16.4 (*s*, Me_3C); –4.6 (*q*, Me_2Si). CI-MS: 155 ([*M*+H]$^+$).

1.2. *(*tert*-Butyl)dimethyl(2-phenylethynyl)silane* (**6b**). Analogeously to **6a**, phenyl acetylene (5.8 ml, 50 mmol), deprotonated with BuLi (60 mmol) and reacted with **4** (5.0 g, 40.9 mmol), gave after distillation (bulb-to-bulb, 100°C/10^{-4} torr) **6b** (5.9 g, 27.5mmol, 82%) as a colorless oil. IR ($CHCl_3$): 3300*w*, 3080*w*, 3060*w*, 3000*w*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2150*s*, 1590*w*, 1490*s*, 1470*s*, 1460*s*, 1440*m*, 1410*w*, 1390*w*, 1360*w*, 1250*s*, 1070*w*, 1025*w*, 1005*m*, 940*w*, 915*w*, 840*s*. ^1H NMR: 7.49–7.29 (*m*, 5 arom. H); 1.01 (*s*, *t*-Bu); 0.19 (*s*, Me_2Si). ^{13}C NMR: 132.0 (*d*, 2

arom. C); 128.3 (*d*, arom. C); 128.2 (*d*, 2 arom. C); 123.2 (*s*, arom. C); 105.7 (*s*, Ph*C*≡); 92.4 (*s*, Si*C*=); 26.1 (*q*, *Me*$_3$C); 16.6 (*s*, Me$_3$*C*); –4.7 (*q*, Me$_2$Si). CI-MS: 217 ([*M*+H]$^+$).

1.3. *(*tert*-Butyl)dimethyl(4-phenylbut-1-ynyl)silane* (**6c**). To a solution of **6a** (0.30 g, 1.95 mmol) in THF (8 ml) was added BuLi (1.5 ml, 2N in pentane) at –80°C. After 1h, a solution of benzyl bromide (0.43 mg dissolved in 2 ml of THF) was added dropwise. The temperature was gradually raised to –60°C (10 min). It was stirred for an additional 1h and quenched at –80°C with saturated aqueous NH_4Cl solution (10 ml). The aqueous layer was extracted with Et_2O, and the combined organic phases were dried over $MgSO_4$ and evaporated. The crude product gave after chromatography (hexane) **6c** (0.38g, 1.56 mmol, 80%) as a colorless oil. IR ($CHCl_3$): 3080*w*, 3060*w*, 3020*m*, 2950*s*, 2925*s*, 2900*m*, 2835*s*, 2180*s*, 1600*w*, 1490*m*, 1470*m*, 1460*m*, 1450*m*, 1425*w*, 1410*w*, 1375*w*, 1360*m*, 1335*w*, 1250*s*, 1120*w*, 1095*w*, 1075*w*, 1040*m*, 1030*m*, 1005*m*, 995*w*, 940*w*, 905*w*, 870*m*, 835*s*, 825*s*, 810*s*, 775*s*, 745*m*, 695*s*, 680*m*, 620*m*. ^{1}H NMR: 7.29–7.15 (*m*, 5 arom. H); 2.87 (*t*, *J* =7.6, PhCH_2); 2.50 (*t*, CH_2C≡); 0.88 (*s*, *t*-Bu); 0.03 (*s*, Me$_2$Si). ^{13}C NMR: 140.5 (*s*, arom. C); 128.4, 128.2 (2*d*, each 2 arom. C); 126.1 (*d*, arom. C); 107.0 (*s*, CH_2C≡); 83.3 (*s*, Si*C*=); 35.1 (*t*, Ph*C*H$_2$); 26.0 (*q*, *Me*$_3$C); 22.0 (*t*, *C*H$_2$C=); 16.4 (*s*, Me$_3$*C*); –4.6 (*q*, Me$_2$Si). CI-MS: 262 ([*M*+NH_4]$^+$).

1.4. *[(Benzyloxy)methyl](*tert*-butyl)methyl(prop-1-ynyl)silane* (**7a**). Analogeously to **6a**, propyne, deprotonated with BuLi (6.0 mmol) and reacted with [(benzyloxy)methyl](*tert*-butyl)(chloro)-dimethylsilane (**5**, 5.0 g, 40.9 mmol), gave after filtration through a plug of silica gel (toluene) **7a** (0.88 g, 35.2 mmol, 86%) as a colorless oil. The product was pure as determined by NMR spectroscopy and used in the next reaction without further purification. IR ($CHCl_3$): 3080*w*, 3060*w*, 3020*w*, 2950*s*, 2922*s*, 2890*m*, 2850*s*, 2810*w*, 2180*s*, 1495*w*, 1470*m*, 1460*m*, 1450*m*, 1390*w*, 1380*m*, 1360*m*, 1250*m*, 1205*m*, 1090*s*, 1072*s*, 1028*s*, 1010*w*, 980*w*, 940*w*, 905*w*, 830*s*, 785*s*, 762*s*, 730*s*, 695*s*. ^{1}H NMR: 7.32–7.24 (*m*, 5 arom. H); 4.45 (*s*, PhCH_2O); 3.23, 3.17 (*AB*, *J* = 12.9, SiCH_2O); 1.84 (*s*, *Me*C=); 0.91 (*s*, *t*-Bu); 0.10 (*s*, MeSi). ^{13}C NMR: 139.1 (*s*, arom. C); 128.45, 127.8 (2*d*, each 2 arom. C); 127.7 (*d*, arom. C); 125.6 (*s*, Me*C*≡); 104.8 (*s*, Si*C*≡); 77.1 (*t*, Ph*C*H$_2$O); 61.32 (*t*, SiCH$_2$O) 26.7 (*q*, *Me*$_3$C); 26.4 (*q*, *Me*C=); 17.0 (*s*, Me$_3$*C*); 5.2 (*q*, MeSi). CI-MS: 278 ([*M*+NH_4]$^+$).

1.5. *[(Benzyloxy)methyl](*tert*-butyl)methyl(2-phenylethynyl)silane* (**7b**). Analogeously to **6a**, phenyl acetylene (1.54 ml, 14.1 mmol), deprotonated with BuLi (14.8 mmol) and reacted with **5** (1.95 g, 7.60 mmol), gave after chromatography (hexane/CH_2Cl_2 1:1) **7b** (2.42 g, 7.52 mmol, 98%) as a colorless oil. IR: 3080*w*, 3060*w*, 3030*m*, 2950*s*, 2930*s*, 2890*s*, 2850*s*, 2810*m*, 2740*w*, 2710*w*, 2160*s*, 1595*w*, 1570*w*, 1490*m*, 1470*m*, 1460*m*, 1440*m*, 1430*w*, 1390*w*, 1380*m*, 1360*m*, 1300*w*, 1250*m*, 1220*m*, 1175*w*, 1155*w*, 1090*s*, 1070*s*, 1025*m*, 1010*m*, 980*w*, 940*w*, 965*w*, 955*w*, 835*s*, 800*m*, 780*s*, 755*s*, 735*s*, 720*m*, 690*s*. ^{1}H NMR: 7.53–7.21 (*m*, 10 arom. H); 4.51(*s*, PhCH_2O); 3.37, 3.31 (*AB*, *J* = 13.0, SiCH_2O); 1.02 (*s*, *t*-Bu); 0.24 (*s*, MeSi). ^{13}C NMR: 138.8 (*s*, arom. C); 132.0, 128.5 (2*d*, each 2 arom. C); 128.2 (*d*, arom. C); 128.1 (*d*, 2 arom. C); 127.5 (*d*, 3 arom. C); 123.0 (*s*, arom. C); 106.8 (*s*, Ph*C*≡); 90.1 (*s*, Si*C*≡); 76.8 (*t*, Ph*C*H$_2$O); 60.9 (*t*, SiCH$_2$O); 26.5 (*q*, *Me*$_3$C); 19.9 (*s*, Me$_3$*C*); –7.5 (*q*, MeSi). CI-MS: 323 ([*M*+H]$^+$).

2. ***Preparation of 1-Iodovinylsilanes.*** — 2.1. *(*E*)-(*tert*-Butyl)(1-iodoprop-1-enyl)dimethylsilane* (**8a**). To a solution of **6a** (2.0 g, 14.0 mmol) in Et_2O (30 ml) was slowly added diisobutylaluminum hydride (DIBAH, 13 ml, 20% in toluene) at 23°C. The mixture was refluxed for 8 h, cooled to –50°C, and dropwise treated with an iodine solution (3.96 g, 15.58 mmol, dissolved in 7 ml of THF). The mixture was allowed to warm to 23°C, and stirring was continued for 2 h before it was quenched with a saturated aqueous NH_4Cl solution (20 ml) at –50°C. The aqueous layer was extracted with Et_2O, and the combined organic pahses were dried over $MgSO_4$ and evaporated. The crude product gave after distillation (bulb-to-bulb, 100°C/10^{-4} torr) **8a** (2.49 g, 8.86 mmol, 68%) as a slightly yellow oil: IR ($CHCl_3$): 3000*m*, 2960*s*, 2930*s*, 2890*s*, 2860*s*, 1590*w*. 1470*m*, 1465*m*, 1445*w*, 1405*w*, 1390*w*, 1360*w*, 1325*w*, 1250*s*, 1110*w*, 1050*w*, 987*w*, 840*s*. ^{1}H NMR: 7.42 (*q*, HC=); 1.72 (*d*, *Me*HC=); 0.99 (*s*, *t*-Bu); 0.31 (*s*, Me$_2$Si). ^{13}C NMR: 153.9 (*d*, HC=); 104.3 (*s*, Si*C*=); 28.3 (*q*, *Me*$_3$C); 22.9 (*s*, Me$_3$*C*); 0.0 (*q*, Me$_2$Si). CI-MS: 283 ([*M*+H]$^+$).

2.2. *(*E*)-(*tert*-Butyl)(1-iodo-2-phenylethenyl)dimethylsilane* (**8b**). Analogeously to **8a**, **6b** (3.0 g, 14.0 mmol), reacted with DIBAH (17.3 ml) and iodine (5.29 g, 20.83 mmol), gave after distillation (bulb-to-bulb, 100°C/10^{-4} torr) **8b** (3.61 g, 10.52 mmol, 75%) as a slightly yellow oil. IR ($CDCl_3$): 3000*m*, 2960*s*, 2930*s*, 2890*s*, 2860*s*, 2160*w*, 1600*w*, 1565*w*, 1490*m*, 1470*s*, 1465*s*, 1445*m*, 1410*w*, 1395*w*, 1365*m*, 1255*s*, 1100*w*, 1070*w*, 1010*m*, 990*w*, 940*w*, 930*w*, 840*s*, 820*s*, 810*s*. ^{1}H NMR: 8.54 (*s*, HC=); 7.29–7.15 (*m*, 5 arom. H); 1.02 (*s*, *t*-Bu); –0.09 (*s*, Me$_2$Si). ^{13}C NMR:

158.9 (*d*, HC=); 142.4 (*s*, arom. C); 129.6 (*d*, 3 arom. C); 129.5 (*d*, 2 arom. C); 111.0 (*s*, SiC=); 29.9 (*q*, Me_3C); 0.0 (*s*, Me_2Si). CI-MS: 345 ($[M+H]^+$).

2.3. *(E)(tert-Butyl)(1-iodo-4-phenylbut-1-enyl)dimethylsilane* (**8c**). Analogeously to **8a**, **6c** (2.24 g, 9.18 mmol), reacted with DIBAH (11.46 ml) and iodine (3.49 g, 13.77 mmol), gave after distillation (bulb-to-bulb, 100°C/10^{-4} torr) **8c** (2.36 g, 6.34 mmol, 69%) as a slightly yellow oil. IR: 3080*w*, 3060*w*, 3020*m*, 2950*s*, 2925*s*, 2890*m*, 2850*s*, 1600*w*, 1580*m*, 1490*m*, 465*m*, 1460*m*, 1450*m*, 1400*w*, 1385*w*, 1360*m*, 1340*w*, 1260*s*, 1250*s*, 1150*w*, 1120*m*, 1080*w*, 1030*w*, 1005*w*, 935*w*, 905*w*, 865*m*, 835*s*, 820*s*, 810*s*, 775*m*, 765*s*, 750*s*, 730*m*, 695*s*, 670*m*. ^{1}H NMR: 7.35 (*t*, *J* = 7.8, HC=); 7.33–7.11 (*m*, 10 arom. H); 2.65 (*m*, PhCH_2); 2.31 (*m*, CH_2HC=); 0.93 (*s*, *t*-Bu); 0.24 (*s*, Me_2Si). ^{13}C NMR: 158.5 (*d*, HC=); 141.9 (*s*, arom. C); 129.6, 129.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 104.4 (*s*, SiC=); 39.1 (*t*, Ph*C*H_2); 36.4 (*t*, *C*H_2HC=); 28.3 (*q*, Me_3C); 19.6 (*s*, Me_3C); 0.0 (*q*, Me_2Si). CI-MS: 390 ($[M+NH_4]^+$).

2.4. *(E)-[(Benzyloxy)methyl](tert-butyl)(1-iodoprop-1-enyl)methylsilane* (**9a**). Analogeously to **8a**, **7a** (0.88 g, 3.38 mmol), reacted with DIBAH (3.60 ml) and iodine (1.12 g, 4.40 mmol), gave after chromatography (hexane/CH_2Cl_2 1:1) **9a** (0.95 g, 2.45 mmol, 72%) as a slightly yellow oil. IR ($CHCl_3$): 3080*w*, 3060*w*, 3020*m*, 2970*s*, 2920*s*, 2825*s*, 2810*m*, 1580*m*, 1490*m*, 1460*s*, 1375*m*, 1360*m*, 1320*w*, 1250*s*, 1205*m*, 1090*s*, 1070*s*, 1025*m*, 1005*m*, 980*w*, 935*w*, 900*w*, 830*s*, 785*s*, 732*s*, 695*s*. ^{1}H NMR: 7.41 (*q*, *J* = 7.4, HC=); 7.37–7.23 (*m*, 5 arom. H); 4.50 (*s*, PhCH_2O); 3,46, 3.40 (*AB*, *J* = 13.0, SiCH_2O); 1.70 (*d*, *J* = 7.4, *Me*HC=); 1.02 (*s*, *t*-Bu); 0.19 (*s*, MeSi). ^{13}C NMR: 154.0 (*d*, HC=); 138.8 (*s*, arom. C); 128.4, 127.8 (2*d*, each 2 arom. C); 127.6 (*d*, arom. C) 99.6 (*s*, SiC=); 77.4 (*t*, Ph*C*H_2O); 63.0 (*t*, SiCH_2O); 27.8 (*q*, *Me*HC=); 20.0 (*q*, Me_3C); 19.1 (*s*, Me_3C); –3.7 (*q*, MeSi). CI-MS: 406 ($[M + NH_4]^+$).

2.5. *(E)-[(Benzyloxy)methyl](tert-butyl)(1-iodo-2-phenylethenyl)methylsilane* (**9b**). Analogeously to **8a**, **7b** (2.28 g, 7.09 mmol), reacted with DIBAH (7.10 ml of a 1.5M solution in toluene) and iodine (3.24 g, 12.77 mmol), gave after chromatography (hexane/CH_2Cl_2 1:1) **9b** (2.65 g, 5.88 mmol, 83%) as a slightly yellow oil. IR: 3080*w*, 3060*m*, 3020*m*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2810*m*, 1600*w*, 1565*w*, 1490*m*, 1470*s*, 1460*s*, 1440*m*, 1405*w*, 1390*w*, 1375*m*, 1360*m*, 1300*w*, 1250*s*, 1200*w*, 1175*w*, 1155*w*, 1105*s*, 1090*s*, 1070*s*, 1025*m*, 1010*w*, 980*w*, 885*w*, 875*w*, 850*w*, 825*s*, 790*s*, 775*m*, 750*s*, 730*s*, 695*s*. ^{1}H NMR: 8.56 (*s*, HC=); 7.35–7.17 (*m*, 10 arom. H); 4.33, 4.27 (*AB*, *J* = 12.1, PhCH_2O); 3.14, 3.01 (*AB*, *J* = 13.0, SiCH_2O); 1.08 (*s*, *t*-Bu); 0.03 (*s*, MeSi). ^{13}C NMR: 157.8 (*d*, HC=); 140.5 (*s*, arom. C); 138.8 (*s*, arom. C); 128.1 (*d*, 2 arom. C); 127.8 (*d*, 3 arom. C); 127.7, 127.5 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 105.6 (*s*, SiC=); 76.8 (*t*, Ph*C*H_2O); 62.2 (*t*, SiCH_2O); 28.4 (*q*, Me_3C); 18.2 (*s*, Me_3C); –4.5 (*q*, MeSi). CI-MS: 468 (10, $[M+NH_4]^+$); 238 (100).

3. ***Preparation of Silylated Allylic Alcohols.*** — 3.1. *(Z)-2-[(tert-Butyl)dimethylsilyl]-1-phenylbut-2-en-1-ol* (**10a**). To a solution of **8a** (2.00 g, 7.09 mmol) in Et_2O (15 ml) was slowly added BuLi (7.8 ml, 2N in pentane) at –80°C. It was stirred for **1** h, and benzaldehyde (2.00 ml, 18.70 mmol, dissolved in 1 ml of Et_2O) was added dropwise. The temperature was slowly raised to –50°C (15 min) and a saturated aqueous NH_4Cl solution (10 ml) was added. The aqueous layer was extracted with Et_2O, and the combined organic phases were dried over $MgSO_4$ and evaporated. The crude product gave after chromatography (hexane/ethyl acetate 25:1) **10a** (1.50 g, 57.47 mmol, 81%) as a colorless oil. IR ($CHCl_3$); 3590*m*, 3420*br.*, 3080*w*, 3060*w*, 2990*w*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2800*w*, 2770*w*, 2700*w*, 1950*w*, 1645*w*, 1610*m*, 1600*m*, 1575*w*, 1490*w*, 1460*m*, 1445*m*, 1400*w*, 1385*w*, 1375*w*, 1360*m*, 1205*w*, 1250*s*, 1200*s*, 1165*w*, 1130*m*, 1090*m*, 1030*m*, 1005*s*, 935*w*, 925*w*, 855*m*, 830*s*, 820*s*. ^{1}H NMR: 7.44–7.24 (*m*, 5 arom. H); 6.47 (*q*, HC=); 5.34 (*s*, C*H*(OH)); 1.87 (*d*, *J* = 6.8, *Me*HC=); 0.91 (*s*, *t*-Bu); 0.12, 0.05 (2*s*, Me_2Si). ^{13}C NMR: 143.7 (*s*, arom. C); 140.61 (*d*, HC=); 140.55 (*s*, SiC=); 128.0 (*d*, 2 arom. C); 127.0 (*d*, 3 arom. C); 77.4 (*d*, CH(OH)); 27.2 (*q*, Me_3C); 18.6 (*q*, *Me*HC=); 18.5 (*s*, Me_3C); –3.2; –3.4 (2*q*, Me_2Si). CI-MS: 245 ($[M+H-H_2O]^+$).

3.2. *(E)-2-[(tert-Butyl)dimethylsilyl]-1-phenylbut-2-en-1-ol* (**10b**). Analogeously to **10a**, **8a** (3.34 g, 11.84 mmol), reacted with BuLi (13.0 ml) in THF at –5°C for 2 h and with benzaldehyde at –5°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **10b** (2.30 g, 8.81 mmol, 74%) as a colorless oil. ^{1}H NMR: 7.50–7.17 (*m*, 5 arom. H); 6.14 (*q*, HC=); 5.77 (*s*, C*H*(OH)); 1.76 (*d*, *J* = 6.8, *Me*HC=); 0.88 (*s*, *t*-Bu); 0.04, –0.08 (2*s*, Me_2Si).

3.3. *(Z)-2-[(tert-Butyl)dimethylsilyl]-1-phenylpent-1-en-3-ol* (**10c**) and *(E)-2-[(tert-Butyl)dimethylsilyl]-1-phenylpent-1-en-3-ol* (**10d**). Analogeously to **10a**, **8b** (1.00 g, 2.91 mmol), reacted with BuLi (2.90 ml) in Et_2O at –80°C for 1 h and with propionaldehyde (0.43 ml, 5.81 mmol) at –80°C for

10 min, gave after chromatography (hexane/ethyl acetate 25:1) **10d** (64 mg, first eluting) and **10c** (632 mg, second eluting) as colorless oils (overall 2.52 mmol, 87%).

Data of **10c**: IR: 3600*m*, 3450*br.*, 3080*w*, 3050*w*, 2950*s*, 2930*s*, 2890*s*, 2880*s*, 2850*s*, 1590*m*, 1485*w*, 1460*m*, 1440*w*, 1400*w*, 1485*w*, 1475*w*, 1460*m*, 1285*w*, 1250*m*, 1230*m*, 1115*m*, 1085*m*, 1065*m*, 1005*m*, 980*w*, 955*m*, 935*w*, 925*w*, 885*w*, 860*m*, 835*s*, 815*s*. ^{1}H NMR: 7.78 (*s*, HC=); 7.38–2.23 (*m*, 5 arom. H); 4.38 (*dd*, *J* = 8.4, 3.6, C*H*(OH)); 1.85–1.59 (*m*, MeCH_2); 1.13 (*t*, *J* = 7.4, *Me*CH_2); 0.98 (*s*, *t*-Bu); –0.04, –0.17 (2*s*, Me_2Si). ^{13}C NMR: 146.3 (*s*, arom. C); 142.5 (*d*, HC=); 140.1 (*s*, SiC=); 128.4, 127.4 (2*d*, each 2 arom. C); 126.7 (*d*, arom. C); 74.9 (*d*, CH(OH)); 31.6 (*t*, Me*C*H_2); 27.6 (*q*, *Me*$_3$C); 18.0 (*s*, Me_3*C*); 11.0 (*q*, *Me*CH_2); –3.5, –3.7 (2*q*, Me_2Si). CI-MS: 259 ([*M*+H–H_2O]$^+$).

Data of **10d**: IR: 3600*br.*, 3480*br.*, 3080*w*, 3050*w*, 3020*w*, 2960*s*, 2930*s*, 2890*s*, 2880*s*, 2850*s*, 2800*w*, 1590*w*, 1570*w*, 1490*m*, 1470*m*, 1460*m*, 1440*w*, 1410*w*, 1390*w*, 1350*w*, 1290*w*, 1250*s*, 1110*m*, 1065*m*, 1030*m*, 1010*m*, 965*m*, 935*w*, 920*w*, 900*w*, 835*s*, 820*s*, 810*s*, 770*s*, 750*m*, 700*s*. ^{1}H NMR: 7.38–7.24 (*m*, 5 arom. H); 6.90 (*s*, HC=); 4.68 (*dd*, *J* = 8.3, 3.2, CH(OH)); 1.69 (*m*, MeCH_2); 1.02 (*s*, *t*-Bu); 0.99 (*t*, *J* = 7.6, *Me*CH_2); 0.30, 0.25 (2*s*, Me_2Si). ^{13}C NMR: 146.5 (*s*, arom. C); 140.4 (*d*, HC=) 138.2 (*s*, SiC=); 128.6, 128.0 (2*d*, each 2 arom C); 126.8 (*d*, arom. C); 73.9 (*d*, CH(OH)); 30.6 (*t*, Me*C*H_2); 27.4 (*q*, *Me*$_3$C); 17.4 (*s*, Me_3*C*); 10.6 (*q*, *Me*CH_2); –3.5 (*q*, Me_2Si). CI-MS: 259 (100 [*M*+H–H_2O]$^+$).

3.4. *(Z)-2-[(*tert*-Butyl)dimethylsilyl]-1,3-diphenylprop-2-en-1-ol* (**10e**). Analogeously to **10a**, **8b** (1.00 g, 2.91 mmol), reacted with BuLi (7.40 ml) in Et_2O at –80°C for 1 h and with benzaldehyde (1.58 ml, 14.83 mmol) at –80°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **10e** (1.80 g, 5.55 mmol, 82%) as a colorless oil. IR: 3750*br.*, 3480*br.*, 3080*w*, 3050*m*, 3020*m*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2150*w*, 1695*m*, 1595*m*, 1580*m*, 1570*w*, 1485*m*, 1465*m*, 1445*m*, 1405*w*, 1385*m*, 1360*m*, 1310*w*, 1250*s*, 1200*w*, 1170*w*, 1085*w*, 1065*m*, 1445*m*, 1405*w*, 1385*m*, 1360*m*, 1310*w*, 1250*s*, 1200*w*, 1170*w*, 1085*w*, 1065*m*, 1025*s*, 1010*s*, 935*w*, 920*w*, 880*w*, 830*s*, 820*s*, 810*s*, 770*s*, 755*s*, 745*s*, 730*w*, 700*s*. ^{1}H NMR: 7.67 (*s*, HC=); 7.49–7.19 (*m*, 10 arom. H); 5.58 (*s*, C*H*(OH)); 0.87 (*s*, *t*-Bu); –0.20, –0.25 (2*s*, Me_2Si). CI-MS: 307 ([*M*+H–H_2O]$^+$).

3.5. *(E)-2-[(*tert*-Butyl)dimethylsilyl]-1,3-diphenylprop-2-en-1-ol* (**10f**). Analogeously to **10a**, **8b** (3.30 g, 9.71 mmol), reacted with BuLi (10.7 ml) in THF at –5°C for 2 h and with benzaldehyde (2.26 mi, 21.34 mmol) at –5°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **10f** (2.50 g, 7.76 mmol, 79%) as a colorless oil. IR ($CHCl_3$): 3600*m*, 3450*br.*, 3080*w*, 3060*m*, 3020*w*, 3000*m*, 2950*s*, 2930*s*, 2890*s*, 2850*s*, 1500*s*, 1650*w*, 1595*m*, 1570*w*, 1490*s*, 1470*m*, 1460*m*, 1450*m*, 1410*w*, 1390*w*, 1360*m*, 1310*w*, 1250*s*, 1215*w*, 1170*m*, 1095*w*, 1065*m*, 1015*s*, 920*w*, 885*w*, 825*s*, 700*s*. ^{1}H NMR: 7.45–7.20 (*m*, 10 arom. H); 7.14 (*s*, HC=); 5.94 (*s*, C*H*(OH)); 0.96 (*s*, *t*-Bu); 0.13, –0.19 (2*s*, Me_2Si). ^{13}C NMR: 143.9 (*s*, arom. C); 142.8 (*s*, arom. C); 141.4 (*d*, HC=); 137.0 (*s*, SiC=); 127.9, 127.7 (2*d*, each. 2 arom. C); 127.6 (*d*, arom. C), 126.8, 126.4 (2*d*, each 2 arom. C); 125.7 (*d*, arom. C); 71.6 (*d*, CH(OH)); 26.9 (*q*, *Me*$_3$C); 17.0 (*s*, Me_3*C*); –3.8, –5.0 (2*q*, Me_2Si). CI-MS: 307 ([*M*+H–H_2O]$^+$).

3.6. *(Z)-2-[(*tert*-Butyl)dimethylsilyl]-4-methyl-1-phenylpent-1-en-3-ol* (**10g**). Analogeously to **10a**, **8b** (1.00 g, 3.16 mmol), reacted with BuLi (3.16 ml) in Et_2O at –80°C for 1 h and with isobutyraldehyde (455 mg, 6.32mmol) at –80°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **10g** (721 mg, 2.49 mmol, 82%) as a colorless oil. ^{1}H NMR: 7.34–7.20 (*m*, 5 arom. H); 6.96 (*s*, HC=); 4.36 (*d*, *J* = 9.1, C*H*(OH)); 1.87 (*m*, Me_2C*H*); 0.99 (*s*, *t*-Bu); 0.94, 0.73 (2*d*, *J* = 6.5, 6.9, *Me*$_2$CH); 0.25, 0.21 (2*s*, Me_2Si). CI-MS: 273 ([*M*+H–H_2O]$^+$).

3.7. *(Z)-2-[(*tert*-Butyl)dimethylsilyl]-1,5-diphenylpent-2-en-1-ol* (**10h**) and *(E)-2-[(*tert*-Butyl)-dimethylsilyl]-1,5-diphenylpent-2-en-1-ol* (**10i**). Analogeously to **10a**, **8c** (2.00 g, 5.38 mmol), reacted with BuLi (4.0 ml) in Et_2O at –80°C for 1 h and with benzaldehyde (0.96 ml, 9.00 mmol) at –80°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **10i** (100 mg, first eluting) and **10h** (1.46 g, second eluting) as colorless oils (overall 4.44 mmol, 83%).

Data of **10h**: IR: 3550*br.*, 3430*br.*, 3880*w*, 3060*w*, 3020*m*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 1600*m*, 1490*m*, 1470*m*, 1450*m*, 1410*w*, 1385*w*, 1360*w*, 1250*m*, 1150*w*, 1110*w*, 1060*w*, 1030*w*, 1005*m*, 940*w*, 915*w*, 890*w*, 835*s*, 820*s*, 810*m*, 775*m*, 760*m*, 745*m*, 700*s*, 675*m*. ^{1}H NMR: 7.41–7.23 (*m*, 10 arom. H); 6.55 (*t*, *J* = 7.8, HC=); 5.40 (*s*, C*H*(OH)); 2.82–2.78 (*m*, PhCH_2); 2.68–2.59 (*m*, CH_2C=); 0.97 (*s*, *t*-Bu); 0.16, 0.07 (2*s*, Me_2Si). ^{13}C NMR: 145.1 (*d*, HC=); 143.5 (*s*, arom. C); 141.5 (*s*, arom. C); 140.1 (*s*, SiC=); 128.4, 128.3 (2*d*, each 2 arom. C); 128.1 (*d*, arom. C); 127.2 (*d*,

2 arom. C); 125.8 (*d*, 3 arom. C); 65.8 (*d*, CH(OH)); 36.2 (*t*, Ph*C*H_2); 34.7 (*t*, *C*H_2C=); 27.0 (*q*, *Me*$_3$C); 18.3 (*s*, Me$_3$*C*); –3.2, –3.1 (2*q*, Me$_2$Si). CI-MS: 335 (60 [*M*+H–H_2O]$^+$).

Data of **10i**: IR: 3570*m*, 3470*br.*, 3080*w*, 3060*m*, 3020*m*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2730*w*, 1700*s*, 1650*w*, 1600*m*, 1580*w*, 1490*m*, 1470*m*, 1460*m*, 1450*s*, 1405*w*, 1385*m*, 1360*m*, 1310*m*, 1245*s*, 1200*m*, 1165*m*, 1100*w*, 1065*w*, 1030*m*, 1005*m*, 965*w*, 940*w*, 925*w*, 880*w*, 820*s*, 810*s*, 770*s*, 745*s*, 725*m*, 700*s*. ^{1}H NMR: 7.39–7.16 (*m*, 10 arom. H); 6.08 (*t*, *J* = 7.4, HC=); 5.62 (*s*, C*H*(OH)); 2.84–2.43 (*m*, PhCH_2CH_2); 0.90 (*s*, *Me*$_3$C); 0.05, –0.09 (2*s*, Me$_2$Si). ^{13}C NMR: 143.5 (*d*, HC=); 142.5 (*s*, arom. C); 141.4 (*s*, SiC=); 134.4 (*s*, arom. C); 128.6, 128.2 (2*d*, each 2 arom. C); 128.0 (*d*, arom. C); 126.6 (*d*, 2 arom. C); 126.0 (*d*, 3 arom. C); 72.4 (*d*, CH(OH)); 35.4 (*t*, Ph*C*H_2); 31.7 (*t*, *C*H_2C=); 27.1 (*q*, *Me*$_3$C); 17.2 (*s*, Me$_3$*C*); –4.0, –4.6 (2*q*, Me$_2$Si). CI-MS: 335 (60 [*M*+H–H_2O]$^+$).

3.8. *(Z)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-phenylbut-2-en-1-ol* (**11a** and **11b**). Analogeously to **10a**, **9a** (0.93 g, 2.40 mmol), reacted with BuLi (2.40 ml) in Et_2O at –80°C for 1 h and with benzaldehyde (0.51 ml, 4.79 mmol) at –80°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **11a** (410 mg, first eluting) and **11b** (200 mg, second eluting) as colorless oils (overall 1.66 mmol, 69%).

Data of **11a**: IR ($CHCl_3$): 3080*w*, 3060*w*, 3359*br.*, 3000*s*, 2920*s*, 2860*s*, 1620*m*, 1465*s*, 1550*s*, 1380*m*, 1360*m*, 1255*s*, 1090*s*, 1060*s* 1030*m*, 1010*s*. 940*w*, 905*w*, 865*w*, 825*s*. ^{1}H NMR: 7.41–7.25 (*m*, 10 arom. H); 6.31 (*q*, *J* = 7.0, HC=); 5.30 (*d*, *J* = 8.2, C*H*(OH)); 4.72 (*d*, OH); 4.27, 4.43 (*AB*, *J* = 11.7, PhCH_2O); 3.25, 2.61 (*AB*, *J* = 12.7, SiCH_2O); 1.88 (*d*, *Me*HC=); 1.02 (*s*, *t*-Bu); 0.16 (*s*, MeSi). ^{13}C NMR: 144.6 (*s*, arom. H); 143.0 (*d*, HC=); 139.7 (*s*, SiC=); 137.2 (*s*, arom. H); 128.3, 127.8 (2*d*, each 2 arom. C); 127.7 (*d*, arom. C); 126.5 (*d*, arom. C); 126.2 (*d*, 3 arom. C); 79.6 (*d*, CH(OH)); 77.1 (*t*, Ph*C*H_2O); 61.9 (*t*, SiCH_2O); 27.8 (*q*, *Me*$_3$C); 18.8 (*s*, Me$_3$*C*); 18.7(*q*, *Me*HC=); –5.8 (*q*, MeSi). CI-MS: 369 (30, [*M*+H]$^+$), 238 (100).

Data of **11b**: IR ($CHCl_3$): 3350*br.* 3080*w*, 3060*w*, 3000*s*, 2930*s*, 2860*s*, 1615*m*, 1495*m*, 1465*s*, 1450*s*, 1380*m*, 1365*m*, 1255*s*, 1090*s*, 1065*s*, 1030*m*, 1010*s*, 940*w*, 905*w*, 865*w*, 825*s*, 700*s*. ^{1}H NMR: 7.39–7.20 (*m*, 10 arom. H); 6.33 (*q*, HC=); 5.33 (*s*, C*H*(OH)); 4.51, 4.46 (*AB*, *J* = 11.8, PhCH_2O); 3.28, 3.17 (*AB*, *J* = 12.7, SiCH_2O); 1.83 (*d*, *J* = 7.2, *Me*HC=); 0.83 (*s*, *t*-Bu); 0.21 (*s*, MeSi). ^{13}C NMR: 142.7 (*s*, arom. C); 141.5 (*d*, HC=); 139.3 (*s*, SiC=); 136.6 (*s*, arom. C); 127.2, 126.8 (2*d*, each 2 arom. C); 126.7 (*d*, arom. C); 126.5, 125.7 (2*d*, each 2 arom. C); 125.6 (*d*, arom. C); 78.1 (*d*, CH(OH)); 76.2(*t*, Ph*C*H_2O); 61.1 (*t*, SiCH_2O); 26.7 (*q*, *Me*$_3$C); 17.8 (*q*, *Me*HC=); 17.3 (*s*, Me$_3$*C*); –6.3 (*q*, MeSi). CI-MS: 369 (30, [*M*+H]$^+$), 238 (100).

3.9. *(E)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-phenylbut-2-en-1-ol* (**11c** and **11d**). Analogeously to **10a**, **9a** (1.40 g, 3.67 mmol), reacted with BuLi (4.0 ml) in THF at –5°C for 2 h and with benzaldehyde (0.90 ml, 7.94 mmol) at –5°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **11c** (333 mg, first eluting) and **11d** (461 mg, second eluting) as colorless oils (overall 2.16 mmol, 60%). Optically active **11c** and **11d** were obtained from (–)-**13** (see 6.2.).

Data of (–)-(*R*$_{Si}$)-**11c**: $[\alpha]_D^{23}$ = –15±2 (c = 1.1 THF). IR: 3390*br.*, 3080*w*, 3060*m*, 3020*m*, 3000*w*, 2960*s*, 2920*s*, 2880*s*, 2850*s*, 2810*m*, 2600*m*, 1765*w*, 1490*m*, 1460*m*, 1445*m*, 1430*m*, 1380*m*, 1360*m*, 1250*m*, 1205*w*, 1185*m*, 1175*m*, 1150*m*, 1085*m*, 1065*s*, 1025*m*, 1010*s*, 980*w*, 940*w*, 920*w*, 900*w*, 875*w*, 865*w*, 825*s*, 810*m*, 795*m*, 745*s*, 720*m*, 700*s*. ^{1}H NMR: 7.49–7.23 (*m*, 10 arom. H); 6.25 (*q*, *J* = 6.9, HC=); 5.76 (*s*, C*H*(OH)); 4.89 (*s*, OH); 4.29, 4.10 (*AB*, *J* = 11.8, PhCH_2O); 3.24, 2.56 (*AB*, *J* = 12.7, SiCH_2O); 1.87 (*d*, *J* = 6.8, *Me*HC=); 1.08 (*s*, *t*-Bu); 0.04 (*s*, MeSi). ^{13}C NMR: 144.5 (*s*, arom. C); 142.3 (*s*, arom. C); 138.1 (*d*, HC=); 137.2 (*s*, SiC=); 128.3, 128.1 (2*d*, each 2 arom. C); 127.8 (*d*, arom. C); 127.7, 126.6 (2*d*, each 2 arom. C); 126.0 (*d*, arom C); 77.0 (*t*, Ph*C*H_2O); 71.4 (*d*, CH(OH)); 61.2 (*t*, SiCH_2O); 27.6 (*q*, *Me*$_3$C); 17.6 (*s*, Me$_3$*C*); 15.3 (*q*, *Me*HC=); –6.6 (*q*, MeSi). CI-MS (isobutane): 351 (10, [*M*+H–H_2O]$^+$), 221(100).

Data of (–)-(*R*$_{Si}$)-**11d**: $[\alpha]_D^{23}$ = –13±2 (c = 0.8, THF). IR: 3570*w*, 3390*br.*, 3080*w*, 3060*w*, 3020*m*, 2960*s*, 2920*s*, 2880*s*, 2850*s*, 1600*m*, 1490*m*, 1470*m*, 1460*m*, 1445*m*, 1380*m*, 1360*m*, 1250*m*, 1205*w*, 1190*w*, 1175*w*, 1140*w*, 1080*m*, 1060*m*, 1025*m*, 1010*m*, 980*w*, 935*w*, 915*w*, 900*w*, 855*w*, 825*m*, 800*m*, 785*m*, 765*m*, 750*m*, 735*m*, 700*s*. ^{1}H NMR: 7.37–7.25 (*m*, 10 arom. H); 6.18 (*q*, HC=); 5.82 (*s*, C*H*(OH)); 4.46, 4.37 (*AB*, *J* = 12.8, PhCH_2O); 4.27 (*s*, OH); 3.19 (*s*, SiCH_2O); 1.88 (*d*, *J* = 6.8, *Me*HC=); 0.69 (*s*, *Me*$_3$C); 0.13 (*s*, MeSi). ^{13}C NMR: 144.0 (*s*, arom. C); 141.8 (*s*, arom. C); 139.4 (*d*, HC=); 137.5 (*s*, SiC=); 128.3, 127.9 (2*d*, each 2 arom. C); 127.7 (*d*, arom. C); 126.4, (*d*, 2 arom. C) 125.8 (*d*, 3 arom. C); 77.4 (*t*, Ph*C*H_2O); 71.5 (*d*, CH(OH)); 61.4 (*t*,

$SiCH_2O$); 27.3 (*q*, *Me*$_3$C); 17.1 (*s*, Me$_3$*C*); 15.6 (*q*, *Me*HC=); –5.8 (*q*, MeSi). CI-MS (isobutane): 351 (10, [*M*+H–H_2O]$^+$), 221 (100).

3.10. *(Z)-4-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2-methylhex-4-en-3-ol* (**11e** and **11f**). Analogeously to **10a**, **9a** (375 mg, 0.97 mmol), reacted with BuLi (2.0 ml) in Et_2O at –80°C for 1 h and with isobutyraldehyde (1.39 mg, 1.93 mmol) at –80°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **11e** (100 mg, first eluting) and **11f** (200 mg, second eluting) as colorless oils (overall 0.90 mmol, 93%).

Data of **11e**: IR ($CHCl_3$): 3400*br.*, 3090*w*, 3070*w*, 3030*w*, 3000*s*, 2960*s*, 2930*s*, 2860*s*, 2820*m*, 1610*m*, 1495*w*, 1465*m*, 1455*m*, 1435*m*, 1380*m*, 1365*m*, 1310*w*, 1255*m*, 1215*w*, 1160*w*, 1125*w*, 1085*m*, 1070*s*, 1030*m*, 1010*m*, 990*w*, 940*w*, 905*w*, 860*w*, 825*m*, 805*m*, 700*m*. ^{1}H NMR: 7.29–7.26 (*m*, 5 arom. H); 6.34 (*q*, HC=); 4.45 (*s*, PhCH_2O); 3.63 (*m*, C*H*(OH)); 3.39, 3.20 (*AB*, *J* = 12.8, $SiCH_2O$); 1.75 (*d*, *J* = 7.0, *Me*HC=); 1.70 (*m*, Me_2CH); 0.97 (*d*, *J* = 6.6, *Me*CH); 0.94 (*s*, *t*-Bu); 0.75 (*d*, *J* = 6.8, *Me*CH); 0.13 (*s*, MeSi). ^{13}C NMR: 140.3 (*d*, HC=); 139.3 (*s*, SiC=); 137.5 (*s*, arom. C); 128.2, 127.9 (2*d*, each 2 arom. C); 127.7 (*d*, arom. C); 84.1 (*d*, CH(OH)); 77.3 (*t*, PhCH_2O); 62.2 (*t*, $SiCH_2O$); 33.1 (*d*, Me_2CH); 27.8 (*q*, *Me*$_3$C); 20.6 (*q*, *Me*HC=); 19.4 (*q*, *Me*CH); 18.7 (*q* and *s*, *Me*CH, Me$_3$*C*); –5.6 (*q*, MeSi). CI-MS: 317 (70, [*M*+H–H_2O]$^+$), 238 (100).

Data of **11f**: IR ($CHCl_3$): 3500*br.*, 3080*w*, 3060*w*, 3010*m*, 3000*s*, 2970*s*, 2920*s*, 2850*s*, 2810*m*, 1610*m*, 1490*w*, 1460*m*, 1450*m*, 1430*m*, 1380*m*, 1360*m*, 1320*w*, 1310*w*, 1250*m*, 1210*w*, 1180*w*, 1160*w*, 1120*w*, 1080*w*, 1030*m*, 1000*m*, 980*w*, 930*w*, 880*w*, 860*w*, 820*s*, 800*m*, 700*m*. ^{1}H NMR: 7.39–7.25 (*m*, 5 arom. H); 6.44 (*q*, HC=); 4.48 (*s*, PhCH_2O); 3.76 (*d*, *J* = 6.9, C*H*(OH)); 3.53, 3.34 (*AB*, *J* = 12.0, $SiCH_2O$); 1.83 (*d*, *J* = 7.0, *Me*HC=); 1.66 (*m*, Me_2CH); 0.97 (*s*, *t*-Bu); 0.94, 0.84 (2*d*, *J* = 6.6, 6.8, *Me*$_2$CH); 0.24 (*s*, MeSi). ^{13}C NMR: 140.8 (*d*, HC=); 139.5 (*s*, SiC=); 138.1(*s*, arom. C); 128.1, 127.7 (2*d*, each 2 arom. C); 127.4 (*d*, arom. C); 83.2 (*d*, CH(OH)); 77.3 (*t*, PhCH_2O); 62.4 (*t*, $SiCH_2O$); 33.8 (*d*, Me_2CH); 27.9 (*q*, *Me*$_3$C); 20.6 (*q*, *Me*HC=); 18.8 (*q*, *Me*CH); 18.7 (*s*, Me$_3$*C*); 17.6 (*q*, *Me*CH); –6.2 (*q*, MeSi). CI-MS: 317 (70, [*M*+H–H_2O]$^+$), 238 (100).

3.11. *(E)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1,3-diphenylprop-2-en-1-ol* (**11g** and **11h**). Analogeously to **10a**, **9b** (1.30 g, 2.89 mmol), reacted with BuLi (3.00 ml) in Et_2O at –80°C for 1 h and with benzaldehyde (0.70 ml, 6.70 mmol) at –80°C for 10 min, gave after chromatography (hexane/ethyl acetate 25:1) **11g** (435 mg, first eluting) and **11h** (565 mg, second eluting) as colorless oils (overall 2.36 mmol, 80%).

Data of **11g**: IR: 3380*br.*, 3080*w*, 3060*m*, 3020*m*,, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2820*m*, 1600*w*, 1590*w*, 1570*w*, 1490*m*, 1470*m*, 1460*m*, 1445*m*, 1430*m*, 1390*m*, 1380*m*, 1360*m*, 1315*w*, 1250*m*, 1220*w*, 1200*w*, 1185*w*, 1175*w*, 1155*w*, 1085*m*, 1065*s*, 1035*s*, 1025*s*, 980*w*, 925*m*, 915*m*, 905*m*, 885*w*, 825*s*, 810*s*, 795*s*, 755*s*, 745*s*, 735*s*, 720*m*, 700*s*. ^{1}H NMR: 7.50–7.14 (*m*, 15 arom. H); 7.13 (*s*, HC=); 5.73 (*d*, *J* = 13.5, C*H*(OH)); 4.91 (*d*, OH); 4.12, 3.90 (*AB*, *J* = 11.7, PhCH_2O); 3.15, 2.41 (*AB*, *J* = 12.8, $SiCH_2O$); 1.08 (*s*, *t*-Bu); 0.07(*s*, MeSi). ^{13}C NMR: 144.6 (*s*, arom. C); 143.6 (*s*, arom. C); 141.5 (*d*, HC=); 137.3 (*s*, SiC=); 137.0 (*s*, arom. C); 128.4, 128.3 (2*d*, each 2 arom. C); 128.2 (*d*, arom. C); 128.1, 127.8 (2*d*, each 2 arom. C); 127.7 (*d*, arom. C); 127.2, 126.8 (2*d*, each 2 arom. C); 126.3 (*d*, arom. C); 77.0 (*t*, PhCH_2O); 71.6 (*d*, CH(OH)); 60.8 (*t*, $SiCH_2O$); 27.6 (*q*, *Me*$_3$C); –6.5 (*q*, MeSi). CI-MS: 413 (10, [*M*+H–H_2O]$^+$), 238 (100).

Data of **11h**: IR: 3580*w*, 3400*br.*, 3080*w*, 3060*m*, 3020*m*, 2960*s*, 2920*s*, 2880*s*, 2850*s*, 1600*w*, 1590*w*, 1570*w*, 1490*s*, 1470*s*, 1460*s*, 1450*s*, 1390*m*, 1370*m*, 1360*m*, 1250*s*, 1200*w*, 1175*w*, 1155*w*, 1090*s*, 1065*s*, 1025*s*, 980*w*, 925*m*, 905*w*, 885*w*, 820*s*, 790*s*, 770*s*, 760*s*, 745*s*, 700*s*. ^{1}H NMR: 7.37–7.23 (*m*, 15 arom. H); 7.21 (*s*, HC=); 5,91 (*s*, C*H*(OH)); 4.48, 4.38 (*AB*, *J* = 11.7, PhCH_2O); 4.33 (*s*, OH); 3.22, 3.12 (*AB*, *J* = 12.6, $SiCH_2O$); 0.82 (*s*, *t*-Bu); 0.18 (*s*, MeSi). ^{13}C NMR: 143.9 (*s*, arom. C); 142.9 (*d*, HC= and probably *s*, arom C); 137.5 (*s*, arom. C); 137.4 (*s*, SiC=); 128.5, 128.3 (2*d*, each 2 arom. C); 128.2 (*d*, arom. C); 128.0, 127.9 (2*d*, each 2 arom. C); 127.7(*d*, arom. C); 127.2, 126.2 (2*d*, each 2 arom. C); 126.0 (*d*, arom. C); 77.3 (*t*, PhCH_2O); 71.8 (*d*, CH(OH)); 61.1 (*t*, $SiCH_2O$); 27.6 (*q*, *Me*$_3$C); –5.4 (*q*, MeSi). CI-MS: 413 (10, [*M*+H–H_2O]$^+$), 238 (100).

4. ***O*-Acetylations.** — 4.1. *(Z)-2-[(*tert*-Butyl)dimethylsilyl]-1-phenylbut-2-enyl trifloroacetate* (**15a**): To a solution of **10a** (200 mg, 0.76 mmol) in pyridine (5 ml) was added trifluoroacetic anhydride (160 mg, 1.15 mmol). It was stirred for 2 h at 23°C and poured on H_2O (10 ml). The aqueous layer was extracted with Et_2O, and the combined organic phases were dried over $MgSO_4$ and evaporated to give **15a** (182 mg, 0.48 mmol, 95%). Further purification proved impossible due to the high instability of the product. ^{1}H NMR: 7.43–7.23 (*m*, 5 arom. H); 7.06 (*s*, CF_3CO_2CH); 6.20 (*q*,

HC=); 1.57 (*d*, *J* = 6.3, *Me*HC=); 1.03 (*s*, *t*-Bu); 0.33, 0.31 (2*s*, Me_2Si). ^{13}C NMR: 180.0 (*s*, C=O); 143.5 (*s*, HC=); 140.1 (*s*, SiC=); 136.9 (*s*, arom. C); 128.4, 128.2 (2*d*, each 2 arom. C); 127.5 (*d*, arom. C); 76.6 (*d*, CF_3CO_2CH); 26.9 (*q*, Me_3C); 21.3 (*q*, *Me*HC=); 15.2 (*s*, Me_3C); –3.6, –4.1 (2*q*, Me_2Si).

4.2. *(Z)-2-[(*tert*-Butyl)dimethylsilyl]-1-phenylbut-2-enyl acetate* (**15b**). Analogeously to **15a**, **10a** (600 mg, 2.29 mmol), reacted with acetic anhydride (351 mg, 3.44 mmol) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **15b** (644 mg, 2.12 mmol, 93%) as a colorless oil. IR ($CHCl_3$): 3080*w*, 3060*w*, 3020*m*, 2960*s*, 2930*s*, 2800*m*, 2860*s*, 1730*s*, 1615*m*, 1495*m*, 1475*m*, 1465*m*, 1455*m*, 1410*w*, 1370*s*, 1330*w*, 1245*s*, 1220*s*, 1180*w*, 1155*w*, 1130*m*, 1080*w*, 1060*m*, 1015*s*, 955*w*, 910*m*, 835*s*, 825*s*, 700*m*. ^1H NMR: 7.32–7.25 (*m*, 5 arom. H); 6.39 (*q*, HC=); 6.37 (*s*, $MeCO_2CH$); 2.09 (*s*, $MeCO_2$); 1.87 (*d*, *J* = 6.7, *Me*HC=); 0.90 (*s*, *t*-Bu); 0.08, 0.02 (2*s*, Me_2Si). ^{13}C NMR: 169.9 (*s*, C=O); 142.0 (*d*, HC=); 140.1 (*s*, SiC=); 136.5 (*s*, arom. C); 128.1, 127.6 (2*d*, each 2 arom. C); 127.5 (*d*, arom. C); 79.2 (*d*, $MeCO_2CH$); 27.2 (*q*, Me_3C); 21.3 (*q*, $MeCO_2$); 18.8 (*s*, Me_3C); 18.6 (*q*, *Me*HC=); –3.4 (*q*, Me_2Si). CI-MS: 245 ($[M+H-MeCO_2H]^+$).

4.3. *(Z)-2-[(*tert*-Butyl)dimethylsilyl]-1-phenylbut-2-enyl chloroacetate* (**15c**). Analogeously to **15a**, **10a** (528 mg, 2.02 mmol), reacted with chloroacetic anhydride (500 mg, 2.92 mmol) in THF/pyridine 5:1 and in the presence of 4-dimethylaminopyridine (cat.) at 23°C for 2 h, gave after filtration through a plug of silica gel (hexane) **15c** (627 mg, 1.77 mmol, 94%) as a colorless oil. IR ($CHCl_3$): 3090*w*, 3060*w*, 3030*w*, 3010*w*, 2960*s*, 2930*s*, 2900*m*, 2880*m*, 2860*m*, 2860*s*, 1750*s*, 1650*w*, 1615*w*, 1495*w*, 1470*m*, 1465*m*,, 1455*m*, 1445*m*, 1410*m*, 1390*w*, 1375*w*, 1360*w*, 1335*w*, 1305*s*, 1260*s*, 1170*s*, 1130*s*, 1100*m*, 1080*m*, 1060*m*, 1010*m*, 960*m*, 895*w*, 835*s*, 820*s*. ^1H NMR: 7.34–7.26 (*m*, 5 arom. H); 6.50 (*q*, HC=); 6.44 (*s*, H_2ClCCO_2CH); 4.07 (*s*, H_2ClC); 1.89 (*d*, *J* = 7.4, *Me*HC=); 0.88 (*s*, *t*-Bu); 0.10, –0.01 (2*s*, Me_2Si). ^{13}C NMR: 167.5 (*s*, C=O); 143.3 (*d*, HC=); 140.4 (*s*, SiC=); 137.1 (*s*, arom. C); 129.6, 129.4 (2*d*, each 2 arom. C); 129.2 (*d*, arom. C); 82.4 (*d*, H_2ClCCO_2CH); 42.5 (*t*, H_2ClC); 28.5 (*q*, Me_3C); 20.2 (*s*, Me_3C); 20.0 (*t*, *Me*CH); –2.0 (*q*, Me_2Si). CI-MS: 259 ($[M+H-H_2ClCCO_2H]^+$).

4.4. *(E)-2-[(*tert*-Butyl)dimethylsilyl]-1-phenylbut-2-enyl acetate* (**15d**). Analogeously to **15a**, **10b** (500 mg, 1.91 mmol), reacted with acetic anhydride (292 mg, 2.86 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **15d** (430 mg, 1.41 mmol, 74%) as a colorless oil. IR: 3080*w*, 3060*w*, 3030*w*, 3000*w*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 2250*w*, 1740*s*, 1600*w*, 1490*w*, 1470*m*, 1460*m*, 1445*m*, 1410*w*, 1390*w*, 1370*m*, 1230*s*, 1200*w*, 1180*w*, 1150*w*, 1120*w*, 1075*w*,, 1020*m*, 980*w*, 940*w*, 935*w*, 910*m*, 835*s*, 825*s*, 810*m*, 770*m*, 735*s*, 700*s*. ^1H NMR: 7.33–7.26 (*m*, 5 arom. H); 6.97 (*s*, $MeCO_2CH$); 6.23 (*q*, HC=); 2.17 (*s*, $MeCO_2$); 1.89 (*d*, *J* = 6.8, *Me*HC=); 0.85 (*s*, *t*-Bu); 0.04,–0.08 (2*s*, Me_2Si). ^{13}C NMR: 170.2 (*s*, C=O); 140.6 (*d*, HC=); 140.0 (*s*, SiC=); 138.5 (*s*, arom. C); 128.1, 127.1 (2*d*, each 2 arom. C); 126.3 (*d*, arom. C); 74.4 (*d*, $MeCO_2CH$); 26.9 (*q*, Me_3C); 21.4 (*q*, $MeCO_2$); 17.3 (*s*, Me_3C); 15.8 (*q*, *Me*CH); –3.8, –4.6 (2*q*, Me_2Si). CI-MS: 245 ($[M+H-MeCO_2H]^+$).

4.5. *(Z)-2-{(*tert*-Butyl)dimethylsilyl}-1-ethyl-3-phenylprop-2-enyl acetate* (**15e**). Analogeously to **15a**, **10c** (200 mg, 0.72 mmol), reacted with acetic anhydride (111 mg, 1.09 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **15e** (191 mg, 0.60 mmol, 83%) as a colorless oil. IR ($CHCl_3$): 3080*w*, 3050*w*, 3020*w*, 2960*s*, 2930*s*, 2880*s*, 2850*s*, 1740*s*, 1590*m*, 1575*w*, 1490*m*, 1460*m*, 1440*m*, 1405*m*, 1365*s*, 1235*s*, 1130*w*, 1090*m*, 1070*w*, 1030*s*, 1015*s*, 955*m*, 935*w*, 910*w*, 895*w*, 860*w*, 835*s*, 820*s*, 810*s*, 770*s*, 750*s*, 730*w*, 700*s*, 685*w*. ^1H NMR: 7.66 (*s*, HC=); 7.36–7.22 (*m*, 5 arom. H); 4.81 (*dd*, *J* = 8.3, 3.5, $MeCO_2CH$); 2.19 (*s*, $MeCO_2$); 1.96–1.68 (*m*, $MeCH_2$); 1.03 (*t*, *J* = 7.4, $MeCH_2$); 0.96 (*s*, *t*-Bu); 0.02, –0.13 (2*s*, Me_2Si). ^{13}C NMR: 170.2 (*s*, C=O); 143.5 (*d*, HC=); 141.4 (*s*, SiC=); 140.0 (*s*, arom. C); 128.4, 127.5 (2*d*, each 2 arom. C); 126.8 (*d*, arom. C); 77.5 (*d*, $MeCO_2CH$); 29.6 (*t*, $MeCH_2$); 27.5 (*q*, Me_3C); 21.3 (*q*, $MeCO_2$); 17.9 (*s*, Me_3C); 10.4 (*q*, $MeCH_2$); –3.0, –3.1 (2*q*, Me_2Si). CI-MS: 259 ($[M+H-MeCO_2H]^+$).

4.6. *(Z)-2-{(*tert*-Butyl)dimethylsilyl}-1-ethyl-3-phenylprop-2-enyl chloroacetate* (**15f**). Analogeously to **15a**, **10c** (400 mg, 1.44 mmol), reacted with chloroacetic anhydride (370 mg, 2.17 mmol) in THF/pyridine 5:1 and in the presence of 4-dimethylaminopyridine (cat.) at 23°C for 2 h, gave after filtration through a plug of silica gel (hexane) **15f** (495 mg, 1.40 mmol, 97%) as a colorless oil. IR: 3080*w*, 3050*w*, 3020*w*, 2960*s*, 2930*s*, 2880*m*, 2850*s*, 1760*s*, 1740*s*, 1590*w*, 1490*w*, 1460*m*, 1440*w*, 1410*w*, 1390*w*, 1380*w*, 1360*w*, 1290*s*, 1260*s*, 1185*s*, 1130*m*, 1090*m*, 1070*w*, 1025*m*, 1010*w*, 960*m*, 925*w*, 910*w*, 895*w*, 860*w*, 835*s*, 820*s*, 810*s*, 770*s*, 750*s*, 730*w*, 700*s*. ^1H NMR: 7.70 (*s*, HC=); 7.38–7.24 (*m*, 5 arom. H); 5.65–5.57 (*m*, H_2ClCCO_2CH); 4.20 (*s*, H_2ClC);

2.11–1.79 (*m*, MeCH_2); 1.09 (*q*, *t*-Bu); 0.97 (*t*, *J* = 7.4, *Me*CH_2); 0.04, –0.10 (2*s*, Me_2Si). ^{13}C NMR: 166.5 (*s*, C=O); 143.9 (*d*, HC=); 140.8 (*s*, SiC=); 137.7 (*s*, arom. C); 128.4, 127.5 (2*d*, each 2 arom. C); 127.0 (*d*, arom. C); 79.7 (*d*, H_2ClCCO_2CH); 41.2 (*t*, H_2ClC); 29.7 (*t*, MeCH_2); 27.5 (*q*, Me_3C); 17.9 (*s*, Me_3C); 10.4 (*q*, *Me*CH_2); –3.1, –3.2 (2*q*, Me_2Si). CI-MS: 245 ([*M* +H–H_2ClCO_2H]$^+$).

4.7. *(Z)-2-{(*tert*-Butyl)dimethylsilyl}-1-ethyl-3-phenylprop-2-enyl dichloroacetate* (**15g**). Analogeously to **15a**, **10c** (300 mg, 1.09 mmol), reacted with dichloroacetyl chloride (240 mg, 1.63 mmol) in THF in the presence of pyridine (0.12 ml, 1.63 mmol) and 4-dimethylaminopyridine (cat.) at 23°C for 1 h, gave after filtration through a plug of silica gel (hexane) **15g** (387 mg, 1.00 mmol, 92%) as a colorless oil. IR ($CHCl_3$): 3080*w*, 3060*w*, 3020*w*, 2960*s*, 2930*s*, 2880*m*, 2860*s*, 1755*s*, 1590*w*, 1490*w*, 1465*m*, 1440*w*, 1405*w*, 1390*w*, 1360*w*, 1290*s*, 1280*s*, 1240*s*, 1220*w*, 1170*s*, 1115*w*, 1090*w*, 1070*w*, 1030*w*, 1010*w*, 910*w*, 900*w*, 860*w*, 835*s*, 820*s*, 700*m*. ^1H NMR: 7.75 (*s*, HC=); 7.38, 7.23 (*m*, 5 arom. H); 6.09 (*s*, HCl_2C); 5.63–5.62 (*m*, HCl_2CO_2CH); 2.71–2.52 (*m*, MeCH_2); 1.13 (*t*, *J* = 7.4, *Me*CH_2); 0.97 (*s*, *t*-Bu); 0.04, –0.09 (2*s*, Me_2Si). ^{13}C NMR: 163.6 (*s*, C=O); 144.2 (*d*, HC=); 140.3 (*s*, SiC=); 139.5 (*s*, arom. C); 128.3, 127.5 (2*d*, each 2 arom. C); 127.0 (*d*, arom. C); 81.2 (*d*, HCl_2CCO_2CH); 64.7 (*d*, HCl_2C); 29.8 (*t*, MeCH_2); 27.4 (*q*, Me_3C); 17.9 (*s*, Me_3C); 10.4 (*q*, *Me*CH_2); –3.20, –3.22 (2*q*, Me_2Si). CI-MS: 259 ([*M* +H–HCl_2CCO_2H]$^+$).

4.8. *(E)-2-{(*tert*-Butyl)dimethylsilyl}-1-ethyl-3-phenylprop-2-enyl chloroacetate* (**15h**). Analogeously to **15a**, **10d** (436 mg (1.58 mmol), reacted with chloroacetic anhydride (405 mg, 2.37 mmol) in THF/pyridine 5:1 and in the presence of 4-dimethylaminopyridine (cat.) at 23°C for 2 h, gave after filtration through a plug of silica gel (hexane) **15h** (535 mg, 1.59 mmol, 96%) as a colorless oil. IR: 3070*w*, 3050*w*, 3020*w*, 2950*s*, 2920*s*, 2880*m*, 2850*s*, 1755*s*, 1730*s*, 1590*w*, 1570*w*, 1490*w*, 1460*m*, 1440*w*, 1410*m*, 1390*w*, 1350*w*, 1360*m*, 1305*s*, 1280*s*, 1250*s*, 1180*s*, 1135*m*, 1075*m*, 1025*w*, 1010*m*, 960*s*, 925*m*, 900*w*, 835*s*, 820*s*, 810*s*, 770*s*, 700*s*. ^1H NMR: 7.39–7.25 (*m*, 5 arom. H); 6.99 (*s*, HC=); 6.00–5.90 (*m*, H_2ClCO_2CH); 4.00, 3.91 (*AB*, *J* = 14.6, H_2ClC); 1.97–1.69, 1.68–1.50 (2*m*, MeCH_2); 1.00 (*s*, *t*-Bu); 0.86 (*t*, *J* = 7.4, *Me*CH_2); 0.30, 0.26 (2*s*, Me_2Si). ^{13}C NMR: 166.6 (*s*, C=O); 143.0 (*d*, HC=); 140.5 (*s*, SiC=); 137.8 (*s*, arom. C); 128.3, 128.2 (2*d*, each 2 arom. C); 127.0 (*d*, arom. C); 78.9 (*d*, H_2ClCCO_2CH); 41.0 (*t*, H_2ClC); 28.7 (*t*, MeCH_2); 27.0 (*q*, Me_3C); 17.6 (*s*, Me_3C); 10.2 (*q*, *Me*CH_2); –3.5, –3.9 (2*q*, Me_2Si). CI-MS: 259 ([*M* +H–H_2ClCO_2H]$^+$).

4.9. *(Z)-2-[(*tert*-Butyl)dimethylsilyl]-1,3-diphenylprop-2-enyl acetate* (**15i**). Analogeously to **15a**, **10e** (600 mg, 1.85 mmol), reacted with acetic anhydride (284 mg, 2.77 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **15i** (598 mg, 1.63 mmol, 88%) as a colorless oil. IR ($CHCl_3$): 3080*w*, 3060*w*, 3030*w*, 3010*w*, 2960*s*, 2930*s*, 2890*m*, 2860*s*, 1730*s*, 1590*m*, 1490*m*, 1470*m*, 1465*m*, 1410*w*, 1390*w*, 1370*s*, 1240*s*, 1220*s*, 1180*w*, 1070*w*, 1050*w*, 1030*m*, 1025*s*, 960*m*, 915*w*, 890*w*, 865*w*, 840*s*, 825*s*, 810*s*, 700*s*. ^1H NMR: 7.63 (*s*, HC=); 7.48–7.24 (*m*, 10 arom. H); 6.64 (*s*, $MeCO_2CH$); 2.15 (*s*, *Me*CO_2); 0.87 (*s*, *t*-Bu); –0.20, –0.27 (2*s*, Me_2Si). ^{13}C NMR: 169.8 (*s*, C=O); 145.4 (*d*, HC=); 140.0 (*s*, SiC=); 138.8 (*s*, arom. C); 139.6 (*s*, arom. C); 128.5, 128.3 (2*d*, each 2 arom. C); 128.2 (*d*, arom. C); 128.0, 127.5 (2*d*, each 2 arom. C); 126.9 (*d*, arom. C); 78.1 (*d*, $MeCO_2CH$); 27.6 (*q*, Me_3C); 21.4 (*q*, *Me*CO_2); 18.0 (*s*, Me_3C); –2.9 (*q*, Me_2Si). CI-MS: 307 ([*M* +H–$MeCO_2H$]$^+$).

4.10. *(E)-2-[(*tert*-Butyl)dimethylsilyl]-1,3-diphenylprop-2-enyl acetate* (**15j**). Analogeously to **15a**, **10f** (260 mg, 0.80 mmol), reacted with acetic anhydride (94 mg, 0.93 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **15j** (239 mg, 0.65 mmol, 81%) as a colorless oil. IR ($CHCl_3$): 3080*w*, 3060*w*, 3030*w*, 3000*w*, 2950*s*, 2930*s*, 2880*m*, 2850*s*, 1730*s*, 1600*w*, 1570*w*, 1490*w*, 1460*w*, 1440*w*. 1405*w*, 1370*m*, 1240*s*, 1100*m*, 1070*m*, 1015*s*, 970*m*, 940*w*, 920*w*, 905*w*, 885*w*, 820*s*, 695*s*. ^1H NMR: 7.33–7.24 (*m*, 10 arom. H); 7.17 (*s*, HC=); 7.11 (*s*, $MeCO_2CH$); 2.08 (*s*, *Me*CO_2); 0.94 (*s*, *t*-Bu); 0.07,–0.12 (2*s*, Me_2Si). ^{13}C NMR: 170.0 (*s*, C=O); 143.7 (*d*, HC=); 139.9 (*s*, SiC=); 139.6 (*s*, arom. C); 137.3 (*s*, arom. C); 128.3, 128.2 (2*d*, each 2 arom. C); 127.3 (*d*, arom. C); 127.2 (*d*, 2 arom. C); 126.3 (*d*, 3 arom. C); 74.7 (*d*, $MeCO_2CH$); 27.0 (*q*, Me_3C); 21.3 (*q*, *Me*CO_2); 17.6 (*s*, Me_3C); –3.3, –4.7 (2*q*, Me_2Si). CI-MS: 307 ([*M* +H–$MeCO_2H$]$^+$).

4.11. *(Z)-2-{(*tert*-Butyl)dimethylsilyl}-1-isopropyl-3-phenylprop-2-enyl dichloroacetate* (**15k**). Analogeously to **15a**, **10g** (300 mg, 1.03 mmol), reacted with dichloroacetyl chloride (226 mg, 1.55 mmol) in THF (2 ml) and pyridine (0.16 ml, 2.0 mmol) and in the presence of 4-dimethylaminopyridine (cat.) at 23°C for 1 h, gave after filtration through a plug of silica gel (hexane) **15k** (375 mg, 0.94 mmol, 90%) as a colorless oil. ^1H NMR: 7.38–7.26 (*m*, 5 arom. H); 7.09 (*s*, HC=); 5.77 (*d*, *J* =

9.9, HCl_2CCO_2CH); 2.05–1.93 (*m*, Me_2CH); 0.96 (*s*, *t*-Bu); 0.88, 0.72 (2*d*, *J* = 6.5, 6.9, Me_2CH); 0.26 (*s*, Me_2Si). CI-MS: 418 (2, $[M+NH_4]^+$), 273 (100, $[M+H-HCl_2CCO_2H]^+$).

4.12. *(Z)-2-{(tert-Butyl)dimethylsilyl}-1.5-diphenylpent-2-enyl acetate* (**15l**). Analogeously to **15a**, **10h** (400 mg, 1.14 mmol), reacted with acetic anhydride (176 mg, 1.70 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **15l** (400 mg, 1.02 mmol, 89%) as a colorless oil. IR (film): 3080*w*, 3060*w*, 3030 *m*, 2950*s*, 2930*s*, 2900*m*, 2850*s*, 1950*w*, 1740*s*, 1605*m*, 1385*w*, 1490*m*, 1470*m*, 1460*m*, 1450*m*, 1410*w*, 1390*w*, 1370*s*, 1235*w*, 1250*s*, 1230*s*, 1180*w*, 1155*w*, 1055*m*, 1030*m*, 1025*s*, 955*m*, 940*w*, 910*w*, 835*s*, 820*s*, 810*s*, 775*m*, 760*m*, 750*s*, 700*s*. ^{1}H NMR: 7.40–7.23 (*m*, 11 H, 10 arom. H, and $MeCO_2CH$) ; 6.45 (*t*, *J* = 7.7, HC=); 2.87–2.76 (*m*, $PhCH_2$); 2.71–2.60 (*m*, CH_2C=); 2.17 (*s*, $MeCO_2$); 0.96 (*s*, *t*-Bu); 0.13, 0.04 (2*s*, Me_2Si). ^{13}C NMR: 169.8 (*s*, C=O); 146.2 (*d*, HC=); 141.4 (*s*, SiC=); 140.0 (*s*, arom. C); 136.0 (*s*, arom. C); 128.5, 128.3 (2*d*, each 2 arom. C); 128.1 (*d*, arom. C); 127.7, 127.6 (2*d*, each 2 arom. C); 125.9 (*d*, arom. C); 79.1 (*d*, $MeCO_2CH$); 36.0 (*t*, $PhCH_2$); 34.7 (*t*, CH_2C=); 27.2 (*q*, Me_3C); 21.3 (*q*, $MeCO_2$); 18.3 (*s*, Me_3C); –3.3 (*q*, Me_2Si). CI-MS: 335 ($[M+H-MeCO_2H]^+$).

4.13. *(Z)-2-{(tert-Butyl)dimethylsilyl}-1.5-diphenylpent-2-enyl chloroacetate* (**15m**). Analogeously to **15**a, **10h** (300 mg, 0.85 mmol), reacted with chloroacetic anhydride (218 mg, 1.28 mmol) in THF/pyridine 5:1 and in the presence of 4-dimethylaminopyridine (cat.) at 23°C for 2 h, gave after filtration through a plug of silica gel (hexane) **15m** (310 mg, 0.72 mmol, 85%) as a colorless oil. IR: 3080*w*, 3060*w*, 3020*w*, 2950*s*, 2920*s*, 2990*m*, 2850*s*, 1760*s*, 1735*s*, 1600*w*, 1490*w*, 1470*w*, 1460*w*, 1450*m*, 1410*w*, 1385*w*, 1360*w*, 1335*w*, 1305*m*, 1280*m*, 1255*s*, 1250*s*, 1165*s*, 1130*m*, 1055*m*, 1030*w*, 1010*w*, 960*m*, 910*w*, 835*s*, 820*s*, 810*m*, 790*w*, 760*m*, 745*m*, 700*s*. ^{1}H NMR: 7.35–7.19 (*m*, 10 arom. H); 6.47 (*t*, *J* = 6.0, HC=); 6.45 (*s*, H_2ClCCO_2CH); 4.08 (*s*, H_2ClC); 2.86–2.69 (*m*, $PhCH_2$); 2.69–2.53 (*m*, CH_2C=); 0.89 (*s*, *t*-Bu); 0.10, –0.04 (2*s*, Me_2Si). ^{13}C NMR: 166.1 (*s*, C=O); 145.9 (*s*, HC=); 141.2 (*s*, SiC=); 138.8 (*s*, arom. C); 135.2 (*s*, arom. C); 128.5, 128.3 (2*d*, each 2 arom. C); 128.2 (*d*, arom. C); 128.1, 128.0 (2*d*, each 2 arom. C); 125.9 (*d*, arom. C); 80.8 (*d*, H_2ClCCO_2CH); 41.1 (*t*, H_2ClC); 36.0 (*t*, $PhCH_2$); 34.6 (*t*, CH_2C=); 27.1 (*q*, Me_3C); 18.3 (*s*, Me_3C); –3.4 (*q*, Me_2Si). CI-MS: 335 ($[M+H-H_2ClCCO_2H]^+$).

4.14. *(Z)-2-{[(Benzyloxy)methyl](tert-butyl)methylsilyl}-1-phenylbut-2-enyl acetate* (**16a**). Analogeously to **15**a, **11**a (150 mg, 0.41 mmol), reacted with acetic anhydride (60 mg, 0.57 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **16a** (140 mg, 0.34 mmol, 86%) as a colorless oil. IR: 3080*w*, 3060*w*, 3000*m*, 2930*s*, 2840*s*, 1730*s*, 1615*w*, 1495*m*, 1460*m*, 1450*m*, 1370*s*, 1240*s*, 1090*s*, 1070*s*, 1015*s*, 955*m*, 900*w*, 825*s*, 700*s*. ^{1}H NMR: 7.29–7.25 (*m*, 10 arom. H); 6.40 (*q*, *J* = 6.4, HC=); 6.35 (*s*, $MeCO_2CH$); 4.39 (*s*, $PhCH_2O$); 3.31, 3.34 (*AB*, *J* = 12.8, $SiCH_2O$); 1.82 (*d*, *J* = 7.3, *Me*CH); 0.88 (*s*, *t*-Bu); 0.05 (*s*, MeSi). ^{13}C NMR: 168.4 (*s*, C=O); 141.0 (*d*, HC=); 138.0 (*s*, SiC=), 137.5 (*s*, arom. H); 133.8 (*s*, arom. C); 126.8, 126.6 (2*d*, each 2 arom. C); 126.3 (*d*, arom. C), 126.2 (*d*, 2 arom. C); 125.9 (*d*, 3 arom. C); 77.2 (*d*, $MeCO_2CH$); 75.8 (*t*, $PhCH_2O$); 60.6 (*t*, $SiCH_2O$); 26.3 (*q*, Me_3C); 20.0 (*q*, $MeCO_2$); 17.6 (*q*, *Me*CH); 17.4 (*s*, Me_3C); –7.7 (*q*, MeSi). CI-MS: 428 (20, $[M+NH_4]^+$), 351 (100, $[M+H-MeCO_2H]^+$).

4.15. *(E)-2-{[(Benzyloxy)methyl](tert-butyl)methylsilyl}-1-phenylbut-2-enyl acetate* (**16b**). Analogeously to **15a**, **11c** (330 mg, 0.90 mmol), reacted with acetic anhydride (138 mg, 1.35 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through a plug of silica gel (hexane) **16b** (300 mg, 0.73 mmol, 82%) as a colorless oil. Optically active (+)-**16b** was obtained likewise from (–)-**11c**. (+)-**16b**: $[\alpha]_D^{23}$ = +8 (c = 0.9, THF). IR: 3080*w*, 3060*w*, 3020*m*, 2950*s*, 2920*s*, 2880*m*, 2850*s*, 2810*m*, 1945*w*, 1800*w*, 1740*s*, 1600*m*, 1580*w*, 1490*m*, 1470*m*, 1460*m*, 1450*m*, 1430*m*, 1370*s*, 1230*s*, 1200*m*, 1180*w*, 1150*w*, 1090*m*, 1070*s*, 1020*s*, 1000*m*, 980*m*, 955*m*, 935*w*, 905*w*, 830*s*, 785*m*, 770*m*, 750*s*, 735*s*, 700*s*. ^{1}H NMR: 7.32–7.25 (*m*, 10 arom. H); 6.90 (*q*, HC=); 4.37 (*s*, $PhCH_2O$); 3.28, 3.13 (*AB*, *J* = 12.8, $SiCH_2O$); 2.07(*s*, $MeCO_2$); 1.84 (*d*, *J* = 6.8, *Me*HC=); 0.87 (*s*, *t*-Bu); 0.12 (*s*, MeSi). ^{13}C NMR: 170.0 (*s*, C=O); 141.3 (*d*, HC=); 139.8 (*s*, SiC=); 139.0 (*s*, arom. C); 137.1 (*s*, arom. C); 128.1, 128.0 (2*d*, each 2 arom. C); 127.4 (*d*, arom. C); 127.2, 127.1 (2*d*, each 2 arom. C); 126.7 (*d*, arom. C); 76.9 (*t*, $PhCH_2O$); 74.4 (*d*, $MeCO_2CH$); 61.6 (*t*, $SiCH_2O$); 27.3 (*q*, Me_3C); 21.3 (*q*, $MeCO_2$); 17.5 (*s*, Me_3C); 16.1 (*q*, *Me*HC=); –6.9 (*q*, MeSi). CI-MS: 351 ($[M+NH_4]^+$).

4.16. *(Z)-2-{[(Benzyloxy)methyl](tert-butyl)methylsilyl}-1-isopropylbut-2-enyl acetate* (**16c**). Analogeously to **15a**, **11f** (170 mg, 0.51 mmol), reacted with acetic anhydride (104 mg, 1.02 mmol) in the presence of 4-dimethylaminopyridine (cat.) at reflux for 2 h, gave after filtration through

a plug of silica gel (hexane) **16c** (182 mg, 0.48 mmol, 95%) as a colorless oil. IR ($CHCl_3$): 3080*w*, 3060*w*, 3020*w*, 2960*s*, 2930*s*, 2890*s*, 2850*s*, 2820*w*, 1725*s*, 1610*w*, 1490*w*, 1460*m*, 1450*m*, 1430*m*, 1365*m*, 1270*m*, 1250*s*, 1220*s*, 1140*w*, 1090*m*, 1070*m*, 1050*w*, 1020*m*, 980*w*, 955*w*, 940*w*, 930*w*, 900*w*, 820*m*. ^{1}H NMR: 7.35–7.24 (*m*, 5 arom. H); 6.39 (*q*, HC=); 5.13 (*d*, *J* = 5.8, $MeCO_2CH$); 4.50, 4.45 (*AB*, *J* = 12.1, $PhCH_2O$); 3.40 (*s*, $SiCH_2O$); 2.02 (*s*, $MeCO_2$); 1.97–1.78 (*m*, Me_2CH); 1.80 (*d*, *J* = 7.4, *Me*HC=); 0.96 (*s*, *t*-Bu); 0.84, 0.83 (2*d*, *J* = 6.8, 6.7, Me_2CH); 0.23 (*s*, MeSi). ^{13}C NMR: 170.2 (*s*, C=O); 141.0 (*d*, HC=); 138.9 (*s*, SiC=); 135.2 (*s*, arom. C); 128.0, 127.3 (2*d*, each 2 arom. C); 127.1 (*d*, arom. C); 82.3 (*d*, $MeCO_2CH$); 77.0 (*t*, $PhCH_2O$); 62.1 (*t*, $SiCH_2O$); 31.6 (*d*, Me_2CH); 27.8 (*q*, Me_3C); 21.2 (*q*, $MeCO_2$); 20.1 (*q*, *Me*HC=); 19.0 (*q*, *Me*CH); 18.8 (*s*, Me_3C); 16.4 (*q*, *Me*CH); –6.2 (*q*, MeSi). CI-MS: 394 (10, $[M+NH_4]^+$), 238 (100).

5. ***Preparation of the Allenes***. — 5.1. General Procedure: To solns. of the corresponding silylated allylic acetates (**15a–15m** or **16a–16c**) in dried DMSO (approx. 0.05–0.10M) was added CsF (4 eq.). It was stirred at the respective temperatures (see *Table 2*) until full conversion of the starting esters (TLC evidence). The solns. were cooled to 0°C and H_2O (approx. 20 ml) was added. The aqueous solns. were extracted with Et_2O, the combined organic phases dried over $MgSO_4$, and carefully concentrated to 1 ml. Chromatography (hexane) of the residues gave the corresponding allenes (exact conditions see *Table 2*).

5.1. *1-Phenylbuta-1.2-diene* (**17a**). ^{1}H NMR: 7.36–7.29 (*m*, 5 arom. H); 6.10 (*dq*, *J* = 6.4, 3.1, Ph*H*C=); 5.55 (*dq*, *J* = 6.4, 7.2, Me*H*C=); 1.80 (*dd*, *J* = 7.2, 3.1, Me). ^{13}C NMR: 205.9 (*s*, =C=); 134.9 (*s*, arom. C); 128.4 (*d*, 2 arom. C) 126.5 (*d*, 3 arom. C); 93.9 (*d*, PhH*C*=); 89.4 (*d*, MeH*C*=); 14.0 (*q*, Me).

5.2. *1-Phenylpenta-1,2-diene* (**17b**). IR: 3100*w*, 3080*w*, 3060*m*, 3030*m*, 2960*s*, 2930*s*, 2870*m*, 2850*m*, 1945*s*, 1800*w*, 1750*w*, 1705*w*, 1675*w*, 1600*m*, 1575*w*, 1495*s*, 1455*s*, 1405*w*, 1375*w*, 1330*m*, 1305*w*, 1295*w*, 1265*w*, 1240*w*, 1195*w*, 1175*w*, 1155*w*, 1115*w*, 1070*m*, 1025*m*, 910*m*, 875*s*, 800*w*, 790*m*, 760*s*, 720*m*, 700*s*, 690*s*. ^{1}H NMR: 7.31–7.15 (*m*, 5 arom. C); 6.16 (*dt*, *J* = 6.3, 3.2, Ph*H*C=); 5.64 (*q*, *J* = 6.3, CH_2HC=); 2.16 (*ddq*, *J* = 6.7, 3.2, 7.4, $MeCH_2$); 1.09 (*t*, *J* = 7.4, $MeCH_2$). ^{13}C NMR: 204.8. (*s*, =C=); 135.1 (*s*, arom. C); 128.5, 126.6 (2*d*, each 2 arom. C); 126.5 (*d*, arom. C); 96.7 (*d*, PhH*C*=); 95.1(*d*, MeH*C*=); 21.9 (*t*, $MeCH_2$); 13.4 (*t*, $MeCH_2$). CI-MS: 145 ($[M+H]^+$).

5.3. *1,3-Diphenylallene*: (**17c**). IR (CH_2Cl_2): 3070*s*, 3060*s*, 3020*s*, 3000*s*, 2950*m*, 2750*w*, 1935*s*, 1895*w*, 1880*w*, 1825*w*, 1805*w*, 1750*w*, 1700*w*, 1670*w*, 1595*s*, 1490*s*, 1450*s*, 1330*w*, 1320*w*, 1305*w*, 1255*s*, 1200*m*, 1095*s*, 1070*s*, 1020*s*, 1010*s*, 910*s*, 875*s*. ^{1}H NMR: 7.45–6.91 (*m*, 10 arom. C); 6.62 (*s*, 2 Ph*H*C=). ^{13}C NMR: 207.8 (*s*, =C=); 133.6 (*s*, 2 arom. C); 128.9, 127.3 (2*d*, each 2 arom. C); 127.0 (*d*, 2 arom. C); 98.4 (*d*, 2 PhH*C*=). CI-MS: 123 ($[M+H]^+$).

5.4. *4-Methyl-1-phenyl-1,2-pentadiene* (**17d**). IR ($CHCl_3$): 2950*s*, 2920*s*, 2870*s*, 2860*s*, 1945*m*, 1600*m*, 1490*m*, 1455*m*, 1375*m*, 1360*w*, 1295*w*, 1250*w*, 1160*m*, 1120*m*, 1070*m*, 1000*w*, 910*w*, 875*m*. ^{1}H NMR: 7.43–7.14 (*m*, 5 arom. H); 6.17 (*dd*, *J* = 6.4, 3.0, Ph*H*C=); 5.59 (*t*, *J* = 6.1, i-Pr*H*C=); 2.47–2.42 (*m*, Me_2CH); 1.10, 1.09 (2*d*, *J* = 6.8, 6.7, Me_2CH).

5.5. *1,6-Diphenyl-1,2-pentadiene* (**17e**). IR: 3100*w*, 3080*m*, 3060*s*, 3030*s*, 2820*s*, 2750*m*, 1950*s*, 1875*w*, 1805*w*, 1745*w*, 1700*w*, 1600*m*, 1495*s*, 1450*s*, 1435*w*, 1405*w*, 1380*w*, 1335*w*, 1310*w*, 1295*w*, 1265*w*, 1245*w*, 1195*w*, 1175*w*, 1155*w*, 1070*m*, 1025*m*, 1000*w*, 910*m*, 875*s*, 840*w*, 775*s*, 760*s*, 745*s*, 730*s*, 720*s*, 700*s*. ^{1}H NMR: 7.39–7.24 (*m*, 10 arom. C); 6.21 (*dt*, *J* = 6.6, 2.9, Ph*H*C=); 5.68 (*q*, *J* = 6.6, CH_2HC=); 2.84–2.74 (*m*, CH_2HC=); 2.51–2.43 (*m*, $PhCH_2$). ^{13}C NMR: 205.2 (*s*, =C=); 141.5 (*s*, arom. C); 134.8 (*s*, arom C); 128.5, 128.4 (2*d*, each 2 arom. C); 128.3 (*d*, arom. C); 126.6, 126.5 (2*d*, each 2 arom. C); 125.9 (*d*, arom. C); 94.9 (*d*, PhH*C*=); 94.3 (*d*, CH_2HC=); 35.3 (*t*, CH_2CH); 30.5 (*t*, $PhCH_2$). CI-MS: 221 ($[M+H]^+$).

6. ***Synthesis of the Optically Active Compounds***. — 6.1. *(R)-(–)-[(Benzyloxymethyl)(*tert*-butyl)methylsilyl] Ethyl Ketone* (–)-**13** and *(R)-(+)-[(Benzyloxymethyl)(*tert*-butyl)methylsilyl] Prop-2-enyl Ether*. To a freshly prepared solution of LDA (1.5 mmol) in THF (5 ml) was added (*R*)-(–)-[(benzyloxy)methyl](*tert*-butyl)methylsilyl methyl ketone [(–)-**12**] (0.30 mg, 1.14 mmol) at –80°C. After 1 h, DMPU (0.85 ml, 7 mmol) was added. It was stirred for an additional 30 min and treated with methyl iodide (0.48 g, 3.38 mmol). The temperature was increased gradually to 23°C (30 min), then it was quenched with a saturated aqueous NH_4Cl solution The aqueous layer was extracted with Et_2O, and the combined organic phases were dried over Mg_2SO_4 and evaporated. The crude product gave after chromatography (hexane/ethyl acetate 35:1) (–)-**13** (0.22 g, 0.79 mmol, 70%)

and (*R*)-{[(benzyloxy)methyl](*tert*-butyl)methylsilyl} propen-2-yl ether (50 mg, 0.18 mmol, 16%) as colorless oils.

Data of (–)-**13**: $[\alpha]_D^{23}$ = –10.9±2 (c = 0.8, THF). IR: 3080*w*, 3060*w*, 3025*w*, 2959*s*, 2925*s*, 2880*s*, 2850*m*, 2810*m*, 1640*s*, 1495*w*, 1460*m*, 1430*w*, 1400*w*, 1390*w*, 1375*m*, 1360*m*, 1320*s*, 1250*m*, 1200*w*, 1095*s*, 1070*s*, 1025*m*, 1010*w*, 980*w*, 940*w*, 900*w*, 825*s*, 805*m*, 775*s*, 735*s*, 595*s*. ^{1}H NMR: 7.38–7.28 (*m*, 5 arom.H); 4.50 (*s*, PhCH_2O); 3.44, 3.38 (*AB*, *J* = 13.0, SiCH_2O); 2.67 (*q*, *J* = 7.2, MeCH_2); 0.96 (*s*, *t*-Bu); 0.95 (*t*, *Me*CH_2); 0.24 (*s*, MeSi). ^{13}C NMR: 138.4 (*s*, arom. C); 128.3, 127.6 (2*d*, each 2 arom. C); 77.3 (*t*, PhCH_2O); 59.4 (*t*, SiCH_2O); 44.0 (*t*, Me*C*H_2); 26.8 (*q*, *Me*$_3$C); 16.7 (*s*, Me$_3$*C*); 5.8 (*q*, *Me*CH_2); –9.7 (*q*, MeSi). CI-MS; 279 ([*M*+H]$^+$).

*Data of (R)-(+)-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]} Propen-2-yl Ether*: $[\alpha]_D^{23}$ = 19.9±2 (c = 0.7, THF). IR: 3080*w*, 3060*w*, 3020*w*, 2990*w*, 2959*s*, 2939*s*, 2890*m*, 2850*s*, 1575*s*, 1495*w*, 1460*m*, 1435*w*, 1390*w*, 1375*m*, 1360*m*, 1250*m*, 1215*s*, 1090*s*, 1070*s*, 1035*s*, 1010*w*, 980*w*, 935*w*, 895*s*, 825*s*, 785*s*, 775*s*, 735*s*, 695*s*, 675*w*. ^{1}H NMR: 7.38–7.25 (*m*, 5 arom. H); 4.72 (*d*, *J* =2.2, HC=); 4.50 (*s*, PhCH_2O); 4.38 (*d*, *J* = 2.2, HC=); 3.51 (*s*, *Me*C=); 3.39, 3.32 (*AB*, *J* = 13.0, SiCH_2O); 0.95 (*s*, *t*-Bu); 0.17 (*s*, MeSi). ^{13}C NMR: 167.1 (*s*, Me*C*=); 138.9 (*s*, arom. C); 128.1, 127.3 (2*d*, each 2 arom. C); 95.7 (*t*, H_2C=); 76.9 (*t*, PhCH_2O); 59.9 (*t*, SiCH_2O); 53.7 (*q*, *Me*C=); 26.9 (*q*, *Me*$_3$C); 16.5 (*s*, Me$_3$*C*); –9.4 (*q*, MeSi). CI-MS: 279 ([*M*+H]$^+$).

6.2. *(–)-(*E*)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl }-1-phenylbut-2-en-1-ol* ((–)-**11c** and (–)-**11d**). To a solution of (–)-**13** (0.18 g, 0.65 mmol) in MeCN (5 ml) was added 2,4,6-triisopropylphenylsulfonylhydrazide (0.23 g, 0.77 mmol) at 23°C. It was stirred for 24 h and the solvent evaporated to give after chromatography (hexane/ethylacetate 25:1) the corresponding hydrazone (0.36 g, 0.64 mmol, 98%) as a colorless oil. $[\alpha]_D^{23}$ = –23±2 (c = 0.9, THF). ^{1}H NMR: 8.0 (*s*, N*H*); 7.41–7.23 (*m*, 5 arom. H); 7.14 (*s*, 2 arom. H); 4.37 (*s*, PhCH_2O); 4.17 (*hept.*, *J* = 6.7, 2 Me$_2$C*H*); **3**.11 (*s*, SiCH_2O); 2.88 (*hept.*, *J* = 6.9, Me$_2$C*H*); 2.88 (*q*, *J* = 7.6, MeCH_2); 1.27–1.19 (*m*, 18H, 3 *Me*$_2$CH); 1.01 (*t*, *J* = 6.7, *Me*CH_2); 0.69 (*s*, *t*-Bu); 0.07 (*s*, MeSi). ^{13}C NMR: 166.7 (*s*, C=N); 153.1 (*s*, arom. C); 151.0 (*s*, 2 arom. C); 138.5 (*s*, arom. C); 132.0 (*s*, arom. C); 128.6, 128.1 (2*d*, each 2 arom. C); 127.4 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.1(*t*, SiCH_2O); 34.1 (*d*, Me$_2$*C*H); 29.7 (*d*, 2 Me$_2$*C*H); 26.6 (*q*, 4 Me$_2$CH); 24.8 (*q*, *Me*$_3$C); 23.5 (*q*, *Me*$_2$CH); 23.0 (*t*, Me*C*H_2); 17.0 (*s*, Me$_3$*C*); 8.9 (*q*, *Me*CH_2); –9.3 (*q*, MeSi). CI-MS: 559 [*M*+H]$^+$

This hydrazone (210 mg, 0.37 mmol) was dissolved in hexane/Et_2O (1:1, 6 ml), and *sec*-BuLi (0.9 ml, 1.3M in pentane) was added at –80°C. It was stirred for 4 h, then the temperature was slowly raised to –10°C (10 min), stirring continued for an additional 15 min, and quenched with benzaldehyde (0.1 ml, 0.82 mmol). Saturated aqueous NH_4Cl solution was added, the aqueous layer extracted with Et_2O, and the combined organic phases were dried over $MgSO_4$ and evaporated. The crude product gave after chromatography (hexane/ethyl acetate 25:1) (–)-**11c** (65 mg, 0.18 mmol) and (–)-**11d** (65 mg, 0.18 mmol) as colorless oils (overall 130 mg, 0.35 mmol, 95%). Characterization see 3.9.

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Received: August 6, 1996 - Accepted: August 14, 1996 - Received in revised camera-ready format: August 16, 1996